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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

WILLIAM FRANCIS, PH.D., F.L.S., F.R.A.S., F.C.S.

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THE CHEMICAL GAZETTE.

No. CCXCIII.—January 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Investigation of the Phenomena of Vegetation.

By M. BOUSSINGAULT.

IN the first portion of the present memoir, the author shows that plants continue to grow as usual in a confined portion of air, without renewal, provided the soil contains all the constituents necessary for their growth. The second part has reference to the question, whether a plant surrounded by air in a state of constant renewal absorbs nitrogen. The third part treats of the amount of nitrogen taken up by plants growing in the open air, but sheltered from rain and removed to a considerable distance from the ground.

I. On the 17th of May, 1854, the author sowed three seeds of the garden cress (*Cresson alénois*) in a flower-pot containing 3 kilograms. of earth, and at the same time three similar seeds were placed in the same quantity of earth, enclosed in a glass vessel capable of containing 68 litres, which was then closed so as to exclude all air. On the 16th of June the plants in the closed space were twice as large as those in the flower-pot, which had remained in the open air. On the 15th of August the plants were collected; the enclosed plants had flowered normally, and bore the usual quantity of ripe fruit.

II. In the second series of experiments the seeds were placed in a soil which had previously been calcined. To this the ashes of various plants were added. The plants vegetated in an air-tight case of plate glass, capable of containing about 104 litres. Air was then constantly drawn in by an aspirator, after passing over pumice-stone moistened with sulphuric acid. By a simple arrangement of the apparatus, carbonic acid was allowed to enter the receiver in such quantity, that the air carried with it from 2 to 3 per cent. of this gas.

The pumice-stone in which the seeds were placed was contained in pots containing 4 decilitres; the pots were previously heated to redness. The ashes were prepared with particular care, in order that no carbon should be mixed with them. The carbon, which is of no consequence in itself, would possess an influence if nitrogenous

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bodies were contained in the ashes. The amount of nitrogen in the ashes was carefully determined; they contain cyanides. The author found in 1 grm. of the ashes of—

Meadow-hay	5	milligrms. of nitrogen.
Ears of corn	5.8	„
Peas	3.1	„
Oats (grain)	7.5	„
Couch-grass	3.5	„

The *mixed ashes* mentioned in the following experiments were those obtained by the combustion of the stems and leaves of beans and lupines. 1 grm. of these ashes contained 0.1 milligrm. of nitrogen. Besides this, the washed ashes of stable-manure were frequently added.

The seeds of beans and lupines employed in the experiments contained the following quantities of nitrogen,—dwarf beans, 4.475; lupines, 5.820 per cent.

1. The experiment lasted two months and a week. A seed weighing 0.337 grm., and consequently containing the amount of nitrogen stated below, was sown on May 12, 1854. The soil consisted of pumice-stone to which 0.05 grm. of mixed ashes were added. On July 19th the plant had eleven leaves, and the cotyledons were withered. In this experiment 37,000 litres of air were passed through the apparatus in which the plant was enclosed.

The result of the first experiment was as follows. In this, as in all the other experiments, A represents the amount of nitrogen found in the plant and in the soil at the conclusion of the experiment, and B the nitrogen contained in the seed from which the plant was raised. In this case no nitrogen was taken up by the plant:—

$$A = 0.0187 \text{ grm.}$$

$$B = 0.0196$$

Loss of nitrogen during growth = 0.0009

2. *Vegetation of a Bean in two months and ten days.*—The seed weighed 0.720 grm. It was sown May 14th, 1854. 0.01 grm. of mixed and 5 grms. of washed ashes were added to the soil.

On June 22nd the plant had six normal dark green leaves. The seed-lobes were strong and very fleshy; they had withered on July 2nd. The plant began to bloom on July 20th, when these leaves had fallen from the stem. On July 25th the plant bore four open flowers, twelve fully-developed leaves of a pale green colour, and three young dark green leaves; the stem was 23 centims. in height. The plant, dried on the water-bath, weighed 2 grms. During its growth, 41,500 litres of air had passed through the apparatus. No nitrogen was absorbed:—

$$A = 0.0325 \text{ grm.}$$

$$B = 0.0322$$

Gain in nitrogen = 0.0003

3. *Vegetation of a Bean in three months.*—Seeds were formed. The seed, when sown on May 14th, 1854, weighed 0.748 grm.

There was added to the soil 0.2 grm. of mixed ashes and 1 grm. of washed ashes.

On June 12th the seed-lobes were strong and fleshy; the plant had six normal leaves, nearly as dark as in garden-beans. The cotyledons were yellow. On July 15th the plant bore two well-formed pods, each 3 centims. in length. After blooming, the leaves had become paler; several had fallen off; there were still twenty-one present, amongst which some were very small. On July 24th one of the pods was very fully developed, but the other had fallen off. On August 12th new leaves made their appearance, and the pod, which was dark green on July 24th, had become yellow. On August 17th the pod was ripe. The stem was 28 centims. in height and 6 millims. in diameter at the base. The pod, which was 6 centims. long and 7 millims. broad, contained two very small white beans, which weighed 6 centigrms. The dry plant with the leaves weighed 2.847 grms. No nitrogen was absorbed:—

$$A = 0.0341 \text{ grm.}$$

$$B = 0.0335$$

$$\text{Gain} = 0.0006$$

4. *Vegetation of a Bean in three and a half months.*—The seed weighed 0.755 grm. It was sown on May 10th. The addition made to the soil was 0.5 grm. of mixed and 1 grm. of washed ashes.

On August 22nd the plant bore two pods, one of which was ripe, the other still green. The ripe pod contained a well-formed white bean, weighing 4 centigrms. The stem was 30 centims. in height. In the course of the experiment, 58,000 litres of air passed through the apparatus. In this case also no nitrogen was absorbed:—

$$A = 0.0329 \text{ grm.}$$

$$B = 0.0339$$

$$\text{Loss} = 0.0010$$

5. *Two Beans vegetated for three months and a week.*—The two seeds weighed 1.510 grm. They were sown on May 12th. The soil had added to it 0.3 of mixed and 3 grms. of washed ashes.

On July 17th the plants had twenty-six leaves and thirteen flowers. On the 25th there were four small dark green pods, and the leaves were very pale. On the 10th of August two of the pods were fully developed; they contained three well-formed seeds, nearly as large as those from which the plants were grown; they weighed 7 centigrms. The dried plants weighed 5.15 grms. During the experiment, 55,500 litres of air passed through the apparatus. Result:—

$$A = 0.0666 \text{ grm.}$$

$$B = 0.0676$$

$$\text{Loss} = 0.0010$$

In this case also there was no absorption of nitrogen.

III. In the following experiments all the preceding arrangements, as regards the soil, the addition of ashes and water, were retained.

But the pots in which the plants were grown were placed so that the wind could move their leaves, whilst the plants were sheltered from rain by a glass apparatus. They stood upon a balcony 10 metres above the ground.

1. *A Bean vegetated for three and a half months in the open air.*—The seed, which weighed 0.78 grm., was sown on June 27th. Manure-ashes were added to the soil. On October 12th the plant bore one pod, containing a single imperfect seed. Result:—

$$A = 0.0380 \text{ grm.}$$

$$B = 0.0349$$

$$\text{Gain} = 0.0031$$

2. *Vegetation of a Bean for three months in the open air.*—A bean (*Haricot flageolet*), weighing 0.537 grm., was sown on May 10th, 1852. Manure-ashes were added to the soil.

On July 4th the plant had six fine flowers; on the 11th the flowers had fallen, without forming pods. Three new flowers appeared on the 22nd. On August 12th, a pod, 8 millims. in length, had been formed. The beans had become withered, and dropped off until there remained only seven. The stem was 24 centims. in length. The plant, with all the leaves, dried in the water-bath, weighed 2.11 grms. Result:—

$$A = 0.0238 \text{ grm.}$$

$$B = 0.0213$$

$$\text{Gain} = 0.0025$$

3. *Vegetation of Oats in three and a half months in the open air.*—The stalks bore grains. Four grains of oats, weighing 0.151 grm., were sown on May 20th, 1852. Manure-ashes were added to the soil. On September 1st the plants had from six to nine leaves, and each of them a lateral shoot; the straws were very straight, and each bore a ripe, well-formed, but very small seed. The five seeds together weighed 2 centigrams. The dry plants weighed 0.67 grm. Result:—

$$A = 0.0051 \text{ grm.}$$

$$B = 0.0041$$

$$\text{Gain} = 0.0010$$

4. *Vegetation of a Lupine in three months.*—The seed weighed 0.368 grm.; it was sown on May 18th, 1853. Manure-ashes were added to the soil. On July 7th the vegetation was considerably advanced; on August 6th the leaves had fallen. The plant had hitherto lost leaves, which were replaced by new ones. On August 22nd the plant had eleven leaves, which had been getting yellow since the 6th. It weighed 1.585 grm.:—

$$A = 0.0256 \text{ grm.}$$

$$B = 0.0214$$

$$\text{Gain} = 0.0042$$

5. *Vegetation of a Dwarf Bean in two and a half months.*—The

plant was watered with water saturated with carbonic acid. The seed weighed 0.655 grm.; sown May 17th, 1853; manure-ashes added to the soil. On July 9th the plant had seven expanded flowers. On August 20th the flowers had produced no fruit. The stalk was 33 centims. in height, and bore fifteen leaves; the cotyledons and seed-lobes had withered, but still adhered. The plant was strong, and weighed 2.72 grms. Result:—

$$A = 0.0270 \text{ grm.}$$

$$B = 0.0293$$

$$\text{Loss} = 0.0023$$

6. *Vegetation of a Lupine in two months and three weeks.*—The seed sown on May 15th, 1854, weighed 0.341 grm. The soil had an admixture of 0.1 grm. of mixed and 2 grms. of washed ashes. The plant was watered with water containing carbonic acid.

On July 23rd this plant had thirteen leaves, of which some were much withered. The cotyledons were withered. On August 12th the older leaves began to drop. The plant was 17 centims. in height, and when dried weighed 1.96 grm.:—

$$A = 0.0229 \text{ grm.}$$

$$B = 0.0200$$

$$\text{Gain} = 0.0029$$

7. *Vegetation of two Lupines in two months.*—The two seeds weighed 0.630 grm.; they were planted June 30th, 1854. 2 grms. of washed ashes were added to the soil. On September 5th each lupine bore eight leaves; the cotyledons were withered; the plants 11 centims. high:—

$$A = 0.0387 \text{ grm.}$$

$$B = 0.0367$$

$$\text{Gain} = 0.0020$$

8. *Vegetation of a Bean in two and a half months.*—Water saturated with carbonic acid. The seed weighed 0.710 grm.; planted May 14th, 1854. The soil had an admixture of 0.1 grm. of mixed and 4 grms. washed ashes. On July 24th the plant had four expanded flowers and eighteen leaves; its height was 29 centims. When dried, it weighed 2.20 grms.:—

$$A = 0.0350 \text{ grm.}$$

$$B = 0.0318$$

$$\text{Gain} = 0.0032$$

9. *Vegetation of Cress in two months.*—Seeds were produced. The seed weighed 0.50 grm., and was sown on July 15th, 1854. The soil had an addition of 0.1 grm. of mixed and 1 grm. of washed ashes. The water given to it was saturated with carbonic acid.

The seed-leaves were evolved on July 24th, and normal leaves appeared on the 30th. On August 6th the seed-leaves were withered; they were taken off and preserved. The plants began to flower on August 18th. The leaves were very small. The flowering went on

from the 18th to the 28th of August; the lower leaves became dry in proportion as the upper ones flourished. On September 15th each stalk bore a very small seed, although the fruit differed but little in size from that of garden-cress:—

$$A = 0.0272 \text{ grm.}$$

$$B = 0.0259$$

$$\text{Gain} = 0.0013$$

These last results of the vegetation of plants in the open air show that the quantity of nitrogen which may be absorbed from the atmosphere by plants is not greater than may be accounted for by errors of determination. It certainly appears that a little nitrogen was taken up. In his memoir the author further refers to the question, whether this nitrogen is derived from the minute organic bodies which float in the air or from carbonate of ammonia. He observed the formation of green spots, produced by minute green Cryptogamia, on the outside of the flower-pots, which were never seen on those excluded from the air. He also saw those green filaments produced in rain-water which had been collected at the beginning of a shower, and kept in a flask. Bineau has observed that these filaments consume all the ammonia of rain-water.

The author concludes with some observations on the part played in vegetation by the nitrogenous body pre-existing in the seed, or that formed by the aid of the manure. He describes the vegetation of a plant from seeds which weighed only $\frac{1}{68}$ milligram., and which must therefore have contained a scarcely ponderable quantity of nitrogen, and finds in the vegetation of this plant a convincing proof that the gaseous nitrogen of the atmosphere is not assimilated by plants.—*Comptes Rendus*, Oct. 2, 1854, p. 601.

On the Occurrence of Leucine and Tyrosine in the Human Liver.

By F. T. FRERICHS and G. STÄDELER.

On the microscopic examination of the liver of a pregnant woman, which was in a state of acute atrophy, Frerichs found, especially in the detritus of the disintegrated cells, numerous acicular crystals, which were in too small quantity for further investigation.

In the year 1853 a woman died in the Jews' Hospital at Breslau, after she had been there for some time under treatment for obstruction of the ductus choledochus; the same crystals were found in the liver of this woman. In this liver also the cells were partially disintegrated; and amongst their remains lay numerous tufts of crystals, together with round globules, composed of concentric layers. The gall-ducts were swelled up with dark brown bile, in which laminae of cholesterine and brown granules were to be seen. From this liver so much material was obtained, that the authors were enabled to examine it further.

They washed the liver, after cutting it up, with water, and ascertained that the watery extract contained distinct portions of leucine and tyrosine. Besides this fact, which is of the highest interest both

in chemistry and physiology, the authors give the following information upon the chemical nature of tyrosine. Stædeler, in his memoir upon acetone, had already expressed the opinion that tyrosine belonged to the salicylic series.

The authors employed the tyrosine obtained by them for the preparation of tyrosinosulphuric acid salts. The tyrosine was poured over with concentrated sulphuric acid, when it acquired a red colour, as is always the case with substances of the salicylic series. It was then heated to 392° F., diluted, and saturated with baryta. The saturated solution solidified on cooling in a gelatinous form; it is decomposed by treatment with alcohol into a crystallizable and an amorphous salt. These two salts were separated by water, in which the amorphous salt is soluble, the crystalline insoluble.

Crystalline Tyrosinosulphate of Baryta, $\text{BaO}, \text{SO}^3 + \text{BaO SO}^2 \text{C}^{18} \text{H}^9 \text{NO}^3 + 2\text{HO}$. At 212° F. the salt loses 2 atoms of water of crystallization, which are expelled simultaneously with 5 atoms of hydrogen and 5 atoms of oxygen from the conjunct. It may be regarded as a conjugate dithionate.

The Amorphous Salt, $\text{BaO}, \text{SO}^3 + \text{BaO}, \text{S}^2 \text{O}^2 \text{C}^{18} \text{H}^3 \text{NO}^2$, when dried at 212° F., gives off the two remaining atoms of oxygen of the conjunct, together with 2 atoms of hydrogen, in the form of water. This salt may be regarded as a conjugate trithionate.

Both salts present reactions similar to those of bodies of the salicylic series. The authors believe, that, like hippuric acid, tyrosine is a conjugate glycine compound, thus,—

$\text{C}^3 \text{H}^5 \text{NO}^4$ glycine + $\text{C}^{14} \text{H}^6 \text{O}^4 = 2\text{HO} + \text{C}^{18} \text{H}^9 \text{NO}^6$ hippuric acid.

$\text{C}^4 \text{H}^5 \text{NO}^4 + \text{C}^{14} \text{H}^8 \text{O}^4$ saligenine = $2\text{HO} + \text{C}^{18} \text{H}^{11} \text{NO}^6$ tyrosine.

The authors did not find leucine or tyrosine in fresh healthy livers. They found them in the liver in smallpox and typhus, and Valentiner has found leucine in the urine under the same circumstances.—Müller's *Archiv für Anat. und Phys.*, 1854, p. 387.

Investigation of Bismuth. By R. SCHNEIDER.

The cupreous bismuth ore analysed by Klaproth occurs near Wittichen in the Black Forest. Klaproth's analysis indicates a loss of 5.52 per cent. The formula of the mineral is consequently uncertain.

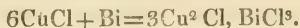
This mineral, both in its external properties and in its chemical relations, exhibits considerable deviation from the cupreous bismuth glance of Saxony. It occurs disseminated in the rock, with scarcely any traces of a crystalline arrangement (at least in the specimens examined by the author); it exhibits an irregular, finely granular fracture, and a slight metallic lustre. The colour of freshly broken surfaces is dark steel-gray, but bright metallic points may be seen even with the naked eye sprinkled here and there in the mass; these are far more distinct under the lens. In consequence of the uniform dissemination of the ore through the mass of the gangue (which in the author's specimens was partly granite, partly heavy spar), its specific gravity could not be exactly determined.

When heated in a glass tube closed at one end, it first of all gives off a very small quantity of water, which is probably to be regarded as hygroscopic water pertaining to the gangue. Stronger heat produces a slight decrepitation, and sulphur and sulphurous acid make their appearance.

The ore is easily and entirely decomposed by boiling nitric acid, with separation of sulphur. It is also briskly attacked by boiling concentrated muriatic acid, with evolution of sulphuretted hydrogen; but the result of this treatment is essentially different according as the access of the air is allowed or prevented. In the latter case, the ore always leaves a granular residue of a metallic lustre, which does not disappear by long boiling; but if, on the other hand, the muriatic acid acts upon the ore in the presence of air, the whole of it, including the gangue, is completely dissolved. The solution obtained by means of muriatic acid with exclusion of air is moreover almost colourless, and exhibits the reaction of protoxide of copper on the addition of ammonia and potash, a proof that the copper contained in the mineral is in the form of basic sulphuret.

The author's analyses of this mineral convinced him that it is a compound of basic sulphuret of copper with tersulphuret of bismuth, in proportions which approximate most closely to the formula $3\text{Cu}^2\text{S}, \text{BiS}^3$. The mineral however always contains an intermixture of metallic bismuth, so that the analytical results, of which the author gives the particulars in his memoir, were very variable.

The author remarked, that when metallic bismuth is boiled with a solution of protochloride of copper which contains free muriatic acid, it is not attacked; but that, on the contrary, when a boiling solution of perchloride of copper (or some other salt of oxide of copper) in muriatic acid is allowed to act upon metallic bismuth, a considerable portion of the latter is dissolved, whilst the cupreous solution, if the bismuth be in excess, is almost entirely decolorized. The resulting fluid contains a compound of perchloride of bismuth with protochloride of copper, probably $3\text{Cu}^2\text{Cl}, \text{BiCl}^3$, for the process can scarcely be otherwise than as shown in the following equation:—



It is evidently the same reaction that takes place when the cupreous bismuth ore is treated with boiling muriatic acid in the presence of air; the protochloride of copper first formed passes rapidly into perchloride under the influence of the atmospheric oxygen, and this acts in the method just mentioned upon the metallic bismuth contained in the ore. If it be desired therefore that the metallic bismuth should remain in the ore, the fluid must be carefully protected from the air during the treatment of the ore with muriatic acid.—Poggendorff's *Annalen*, xciii. p. 305.

On Iodide of Amyle, and its Action upon Alloy of Tin and Sodium.

By A. GRIMM.

The principal object of the author's experiments was to ascertain the radicals which are produced by the action of an alloy of tin and

sodium upon iodide of amyle. The new radicals obtained correspond in part with the stannæthyles; the radical $\text{Sn}^+ \text{A}\mu^3$, representing æthstannmethyle, could not be prepared, whilst another one, $\text{Sn}^2 \text{A}\mu^4$, was obtained, to which there is nothing to correspond in the series of stannæthyles. Amyle, $\text{C}^{10} \text{H}^{11}$, being represented by $\text{A}\mu$, the radicals obtained are as follows:—

- | | |
|--|--|
| 1. $\text{Sn}^2 \text{A}\mu$, bistannamyle. | 4. $\text{Sn}^2 \text{Am}^3$, methstannamyle. |
| 2. $\text{SnA}\mu$, stannamyle. | 5. $\text{Sn}^2 \text{A}\mu^4$, methstannbiamyle. |
| 3. $\text{Sn}^2 \text{A}\mu^2$, methylenstannamyle. | |

All these bodies form fatty slimy masses, which are insoluble in water, but readily soluble in æther. In alcohol they are less soluble in proportion to the quantity of tin they contain. Bistannamyle is apparently quite insoluble; stannamyle and methylenstannamyle are very difficult of solution. Methstannamyle is more soluble, and methstannbiamyle still more so. The two last are always of a pale yellowish colour.

When exposed to the air, these radicals do not fume or attract oxygen with ignition; they have no particular odour. When rubbed between the fingers, however, they evolve the same odour that is communicated to the fingers by rubbing tin. Fuming nitric acid oxidizes these bodies very violently, with detonation; but no ignition takes place as a general rule.

The ætherial or alcoholic solution is oxidized when left to evaporate in the air; the oxide formed is immediately deposited in the form of a white powder. With the halogens the radicals become violently heated, even to boiling. Ammonia separates the radicals from their compounds. Their solutions, nevertheless, have a strong alkaline reaction.

The radicals of stannamyle are distinguished from the stannmethyles and stannæthyles by their being inodorous, whilst the latter are distinctly characterized by their odour. Another distinction is, that the stannamyles have very little tendency to crystallization; only the haloid compounds crystallize. Lastly, the stannamyles and their compounds are not volatile. The properties of the oxides and chlorides are as follows:—

Bistannamyle, $\text{Sn}^2 \text{A}\mu$, has an oxide which is obtained in a turpentine-like, transparent mass, becomes brittle when cold, is but sparingly soluble in absolute alcohol, and dissolves readily in æther, or in a mixture of æther and alcohol.

The *Chloride*, $\text{Sn}^2 \text{A}\mu, \text{Cl}$, is a thick transparent mass, which is soluble in æther and alcohol. The sulphate is very similar.

Oxide of Stannamyle, $\text{SnA}\mu, \text{O}$, is a dazzling white powder, which is quite inodorous, and nearly insoluble in æther; boiling alcohol dissolves a little of it, and the solution has a slight alkaline reaction.

Chloride of Stannamyle is a thick transparent oil at $59^\circ\text{--}68^\circ \text{F.}$, which solidifies at $39^\circ\text{--}41^\circ \text{F.}$ into a crystalline mass. It has a weak camphor-like smell, and a fatty feel; it burns with a pale flame, edged with green. It is soluble in alcohol and æther.

The *Sulphate* is an amorphous white powder, soluble in æther and water, but difficult of solution in alcohol.

Oxide of Methylenstannamyle, $\text{Sn}^2 \text{Am}^2, \text{O}$, is exactly like that of the preceding body.

The *Chloride* crystallizes from its alcoholic solution in distinct columnar crystals. It is difficult of solution in alcohol, and may consequently be separated from chloride of stannamyle by means of alcohol. At 157°F . it fuses into an oleaginous mass, which solidifies in a crystalline form on cooling. The *sulphate*, when obtained by the evaporation of the alcoholic solution, dries to an amorphous, transparent, white mass, which when pounded forms a dazzling white powder. At about 212°F . this shrinks up into a resinous mass.

Oxide of Methstannamyle, $\text{Sn}^2 \text{Ap}^3, \text{O}$, is a transparent, thick, oily mass. It may easily be obtained by shaking the chloride with a little alcoholic solution of potash, and then adding a large quantity of water. The ætherial solution of the oxide then separates.

The *Chloride* is a transparent oil, of a slight yellow colour, insoluble in water, but readily soluble in alcohol; it is thrown down from its alcoholic solution by water. The *sulphate* forms an amorphous transparent mass.

Methstannbiamyle remains dissolved in alcohol, whilst the other radicals separate from the alcoholic solution on cooling; it may be thrown down by the addition of water.

Oxide of Methstannbiamyle, $\text{Sn}^2 \text{Ap}^4, \text{O}$, is obtained by mixing a weak solution of potash with the alcoholic solution of the radical, and then adding æther and water. In this manner an ætherial solution of the oxide is obtained; and by its evaporation the pure oxide forms a perfectly colourless, thinly fluid oil, which is readily soluble in alcohol. The solution is strongly alkaline; the oxide itself has a pleasant odour, resembling that of jasmine.

Chloride of Methstannbiamyle is a colourless oil, which dissolves even in hydrated alcohol; a great addition of water throws it down.

The *Iodide* may be obtained in a crystalline form at a low temperature; it fuses easily into an oily fluid, which possesses all the properties of a fatty oil.

The iodide of amyle employed in these experiments had a specific gravity of 1.4956 at 68°F .; it boiled at 301°F . This boiling-point differs greatly from that calculated by comparison with iodide of æthyle. The iodide of amyle must be as pure as possible; if it be contaminated with amylic alcohol, this mixes with the radicals, and it is then very difficult to separate from them.

The author proceeded in the following way in the preparation of the bodies just mentioned. From $2\frac{1}{2}$ to 3 oz. of alloy of tin and sodium were pounded quickly in an iron mortar, with the mixture of small quantities of sand, the quantity of which was gradually increased until its weight was about double that of the alloy employed; this must all be done as quickly as possible. The mixture is then put into a glass retort capable of containing about 5 or 6 oz., and sufficient iodide of amyle is added to it to convert the whole into a gelatinous mass. The retort is then connected with a distilling-

tube, and the mixture allowed to stand for some minutes. If no reaction be observed to take place at the ordinary temperature, which is generally the case, the action must be assisted by heat, and for this purpose the retort is placed upon the water-bath. It is to be removed as soon as the reaction commences, for the reaction then goes on so rapidly by itself, that the heat evolved during the process distils over all the excess of iodide of amyle. When the reaction is completed, the retort is to be closed air-tight whilst still hot. When completely cooled, the contents of the retort appear as a dry, yellow, pulverulent mass. This is now emptied into a flask nearly full of æther, then shaken several times, and the whole left standing until the æther separates in a perfectly clear state. The apparatus need not be air-tight during this process. The ætherial solution is poured into another flask, and the residue again treated with æther; this is repeated as long as the extraction of the residue appears to have any result. The deep red, transparent, ætherial solution, which gradually loses its colour when exposed to the air, with separation of a white powder, is put into a large retort and mixed with about one-eighth of anhydrous alcohol; the æther is then completely distilled off. At the bottom of the retort there is now a deep red, slimy, resinous mass, from which the hot, yellow, alcoholic solution is immediately poured and well closed up from the air. During cooling a yellowish thick mass also separates from this; the supernatant alcoholic fluid is perfectly colourless.

The author then examined,—1st, the substances contained in the cold alcoholic fluid; 2nd, the mass deposited from the hot alcoholic solution during cooling; and 3rd, the red resinous substance deposited during the distillation of the æther.

1. The substances contained in the cold alcoholic fluid are the three radicals, *stannamyle*, *methylenstannamyle* and *methstannbi-amyle*.

2. In the mass separated during the cooling of the preceding is a mixture of *methylenstannamyle* and *methstannamyle*.

3. The red resinous mass is a mixture of $\text{Sn}^2\text{A}\mu$ with $\text{SnA}\mu$, $\text{Sn}^2\text{A}\mu^2$ and $\text{Sn}^2\text{A}\mu^3$.

The method by which the author effected the separation of these bodies is very troublesome. If it be not required to obtain the radicals themselves, the two following methods may be employed, which lead more rapidly to the desired result; by the first of these the oxides are obtained, by the second the radicals are separated partly as oxides, partly as chlorides.

1. The ætherial solution of the mixed radicals, obtained by the extraction of the mass formed by the action of iodide of amyle upon alloy of tin and sodium, is mixed with alcohol and the æther distilled off. After cooling, the alcoholic solution is separated from the deposit and saturated with iodine; the compound $(\text{Sn}^2\text{A}\mu^4)\text{I}$ is then extracted by æther. The radical of this compound remains entirely in the alcoholic solution. The separated mass is then dissolved in æther, the ætherial solution saturated with iodine, the æther distilled off, and the residue dissolved in absolute alcohol.

The alcoholic solution is shaken with a little solution of potash, which however must not be employed in too great excess; by this a white salve-like mass is precipitated. This is a mixture of $(\text{Sn}^2 \text{A}\mu) \text{O}$, $(\text{Sn}^2 \text{A}\mu^2) \text{O}$ and $(\text{SnA}\mu) \text{O}$, whilst the oxide of $\text{Sn}^2 \text{A}\mu^3$ remains for the most part dissolved in the alcohol. Nevertheless a portion of this oxide occurs in the mixture just referred to. The precipitate is separated from the dissolved portion and treated with æther. $(\text{SnA}\mu) \text{O}$ and $(\text{Sn}^2 \text{A}\mu^2) \text{O}$ remain undissolved, whilst $(\text{Sn}^2 \text{A}\mu) \text{O}$ and $(\text{Sn}^2 \text{A}\mu^3) \text{O}$ dissolve in the æther.

The separation of the oxides in the undissolved portion is best effected by means of sulphuric acid. But if the quantity be sufficient, the two oxides may be dissolved in alcohol and a little muriatic acid, and the solution left to spontaneous evaporation. $(\text{Sn}^2 \text{A}\mu^2) \text{Cl}$ then crystallizes first. The æther is distilled from the dissolved portion, and the residue treated with cold alcohol, which leaves the greater part of the $(\text{Sn}^2 \text{A}\mu) \text{O}$ undissolved, whilst the $(\text{Sn}^2 \text{A}\mu^3) \text{O}$ dissolves.

When the oxides are obtained, the preparation of the salts presents no further difficulties. Complete separation however cannot be effected except in operating upon rather large quantities. The cause of this is, that even the oxides $(\text{SnA}\mu) \text{O}$ and $(\text{Sn}^2 \text{A}\mu^2) \text{O}$ are not perfectly insoluble in alcohol. The same is the case also with the oxide $(\text{Sn}^2 \text{A}\mu) \text{O}$, so that small quantities of the different radicals are always mixed with the others, for which reason fresh separations must always be performed. The two first-mentioned compounds, $(\text{SnA}\mu) \text{O}$ and $(\text{Sn}^2 \text{A}\mu^2) \text{O}$, are most readily obtained in a pure state, and next to these $(\text{Sn}^2 \text{A}\mu) \text{O}$. On the other hand, the preparation of the pure oxide $(\text{Sn}^2 \text{A}\mu^3) \text{O}$ is attended with many difficulties, as it has the power of dissolving the others.

2. A little alcohol is added to the ætherial solution of the mixed radicals, and the solution is allowed to evaporate in the air. The radicals become oxidized, and the oxides $(\text{SnA}\mu) \text{O}$ and $(\text{Sn}^2 \text{A}\mu^2) \text{O}$ separate. The others remain dissolved. The solution is then evaporated and the residue again treated with alcohol, which dissolves the oxides of $\text{Sn}^2 \text{A}\mu^3$ and $\text{Sn}^2 \text{A}\mu^4$, but leaves that of $\text{Sn}^2 \text{A}\mu$ for the most part undissolved. As the first two have almost similar properties, their separation can scarcely be effected, but the corresponding chlorides may be separated in the following manner:—The alcoholic solution of the oxides is saturated with muriatic acid; if water be then added in drops, the compound $(\text{Sn}^2 \text{A}\mu^3) \text{Cl}$ separates at the commencement almost in a state of purity, whilst the compound $(\text{Sn}^2 \text{A}\mu^4) \text{Cl}$ is tolerably soluble even in watery alcohol. —*Journ. für Prakt. Chem.*, lxii. p. 385.

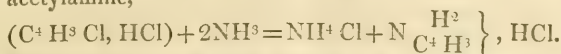
On the Substitution of the Aldehyde Radicals in Ammonia.

By J. NATANSON of Warsaw.

Starting from the idea that the so-called *negative radicals* might be substituted in ammonia, as had been done with the *positive radicals* by Hofmann, M. Natanson tried to produce an iodide of acetylene corresponding to iodide of æthylene, by acting on aldehyde with iodine and phosphorus, and submitting the mixture to distillation.

The greater part of the distillate consisted of iodide of æthyle, and the rest contained a body soluble in water, which gave with nitrate of silver a yellow precipitate, reduced on heating oxide of silver, and evolved a strong smell of aldehyde. All attempts to purify it were fruitless, and an analysis gave results disagreeing with the composition of iodide of acetylene.

Oil of olefant gas can be considered as chloride of acetylene and hydrochloric acid, $C^4 H^4 Cl^2 = C^4 H^3 Cl, HCl$; and on this view ought to give with ammonia, chloride of ammonium and hydrochlorate of acetilamine,—



Oil of olefant gas was heated with a concentrated watery solution of ammonia in a sealed tube, for six hours, at $212^\circ F.$, but no action took place; heated at $302^\circ F.$, after several hours, the oil of olefant gas was absorbed by the excess of ammonia, and the whole was changed into a homogeneous, watery, yellow liquid, which on evaporation over SO^3 deposited crystals of chloride of ammonium. The mother-liquor did not crystallize, but dried to an orange-yellow, tough, gummy mass. On distilling the mother-liquor with lime, pure water containing traces of ammonia went over (evidently resulting from a little adhering chloride of ammonium). If any base therefore were present, it must be a non-volatile one; and a fresh portion of the mother-liquor was treated with oxide of silver, and evaporated to dryness to drive off the ammonia. On treating the mass with water, an alkaline liquid was obtained, which contained in solution oxide and chloride of silver. To separate these, sulphuretted hydrogen was passed through, the sulphide of silver filtered off; the filtrate, after driving off the excess of HS , neutralized with SO^3 ; the sulphate formed decomposed with caustic baryta; and, after evaporation to dryness, the base was dissolved out with alcohol.

Neither a single nor a double salt of the base could be obtained crystallized; hence its purification is extremely difficult. The best way is to treat the aqueous solution of the base with alcohol, when white flocks precipitate, which dry into tough, yellow, gummy masses, extremely difficult to dry, and which when dry are highly hygroscopic.

These properties very much increase the difficulties of the analysis,

The sulphate gave on analysis 40.9 per cent. SO^3 ; the formula $(C^4 H^6 N) O, SO^3$ requires 43.47 per cent.

The precipitate produced in a solution of the base by chloride of platinum forms a yellow tough mass, very difficult to wash. The analysis of this gave 38.22 per cent. platinum. The formula $C^4 H^6 NCl + PtCl^2$ requires 39.57 per cent.

Although from the properties of the body a perfect agreement of the analytical results with the formulæ was hardly to be expected, a further confirmation of the formula appeared necessary; this was sought for in a determination of the relation of carbonic acid to nitrogen by Liebig's method. The formula $N \left. \begin{matrix} C^4 H^3 \\ H^3 \end{matrix} \right\} O$ requires a

proportion of nitrogen to carbonic acid of 1 : 4 ; by experiment the relation was found to be 1 : 3.91.

After these determinations of the empirical formula, two reactions were found, which established its rational composition.

When the chloride of the base is warmed with nitrite of silver, and a few drops of SO^3 added, a brisk evolution of aldehyde is perceived, thus:— $\text{N} \begin{smallmatrix} \text{C}^4 \text{H}^3 \\ \text{H}^3 \end{smallmatrix} \} \text{NO} + \text{NO}^3 = \text{C}^4 \text{H}^3 \text{O}, \text{HO} + 2\text{N} + 2\text{HO} ;$ in this way aldehyde is regenerated, just as by a similar treatment carbolic acid is obtained from aniline.

When the base or any of its salts are boiled with nitrate of silver, metallic silver is deposited.

The base separated as above from the sulphate is a yellowish tough mass, without smell, easily soluble in water or alcohol ; its solution is strongly alkaline, and its taste feebly so. It easily expels ammonia from its salts, and is itself expelled by æthylamine ; it absorbs CO^2 from the atmosphere. Does not dissolve alumina.

Its chloride gives with the chlorides of mercury, platinum and gold, uncrystallizable precipitates. Its chloride is distinguished by its not being precipitated from the aqueous solution by alcohol, which the other salts are.

All the salts are very hygroscopic, and are all insoluble in æther.

The author concludes from this investigation, that the base is not a substituted ammonia, but a substituted oxide of ammonium. He points out the great similarity of this base and of the bases formed by Hofmann, in which *four* equivalents of hydrogen are substituted. The ammonium theory is the only correct explanation, and ammonia and substituted ammonias are merely secondary volatile products of decomposition.

It is very probable, that, in a similar manner to that already given, an entire series of *similar non-volatile* artificial bases may be prepared, by the action of the higher homologues of hydrochlorate of chloride of acetylene. Cahours had failed in preparing the compounds in this manner, from having only employed a temperature of 212°F ., since the action of hydrochlorate of chloride of acetylene in solution on ammonia only takes place at 302°F .

Possibly other equivalents of acetylene or its homologues might be replaced in ammonia ; and these compounds, by treatment with the haloid compounds of the alcohol radicals, might give rise to new non-volatile alkaloids.

The author is engaged with the investigation of this subject.—*Ann. der Chem. und Pharm.*, vol. xcii. p. 48.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Smelting of Pyritic Ores containing small proportions of Silver and Copper with a large proportion of Zinc. By Prof. PLATTNER.

WHEN pyritic ores, consisting chiefly of iron pyrites, and containing small proportions of silver and copper, are smelted in a partially

roasted state in blast-furnaces, together with the fluxes suitable for producing a proper kind of slag, that a copper matte may be obtained in which the per-centage of silver and copper is sufficiently high for extraction, it is possible to remove by volatilization a tolerably large per-centage of zinc, originating from zinc blende mixed with the ore, and to produce a matte possessing all the requisites for treatment with lead, by melting, for example, with argentiferous lead ore and such silver ores as consist chiefly of earthy substances. When the melting is conducted in a furnace with open breast, and the blast sent in a horizontal direction into the melting-chamber, the zinc resulting from the decomposition of the zinc blende by the carbon of the fuel, is driven off in vapour through the breast of the furnace, where it burns with a greenish flame, and is converted into oxide of zinc. Even if a portion of the zinc should rise in vapour into the shaft of the furnace, and again combine with the sulphur present there in vapour, the sulphide would, in the continuous working of the furnace, be mechanically carried into the melting-chamber again in charging the furnace, and decomposed in the same manner into zinc and sulphide of carbon; so that when the ore is very poor in copper, a matte would be obtained presenting, after removal from the furnace and cooling, an orange-yellow fracture with very slight lustre, and consisting chiefly of $(\text{Fe}^2\text{S}, \text{Cu}^2\text{S})^n \text{FeS}$, containing lead as well as silver if the ore is plumbiferous. The amount of zinc is seldom 3 per cent., unless the ore contain a very preponderating quantity of zinc blende.

A very different result is obtained when pyritic ores containing small proportions of silver and copper with a large amount of zinc are smelted in a partly roasted and partly raw state in a reverberatory furnace. The sulphide of zinc is not then decomposed, and passes for the greater part into the matte; so that when this is removed from the furnace and cooled, it presents considerable hardness, a granular micaceous fracture of a black colour and slight lustre. The amount of zinc in such a matte may be as great as 20 per cent., and even more. The fusibility and cohesion of the melted matte are diminished in proportion as the sulphide of zinc increases.

The matte containing silver and copper, together with a large amount of zinc, differs from that containing but a small proportion of this metal in being far more difficult to roast, on account both of the greater compactness of the fragments, and of the much slower oxidation of sulphuret of zinc than of sulphuret of iron at the ordinary roasting temperature; so that the whole of the sulphuret of iron in a matte may be oxidized, and a considerable proportion of sulphuret of zinc be left unaltered, unless the conditions under which the roasting is effected are peculiarly favourable.

In the subsequent treatment of the roasted matte, together with roasted argentiferous lead ore and poor silver ore, the presence of zinc would be prejudicial to the result, and interfere with the operation, because the reduced zinc cannot be removed, as in the first melting below the furnace-breast, without a considerable loss of lead; while the zinc present in the state of oxide and sulphate

would give rise to the formation of scoria, and render the working of the furnace irregular. Moreover, a large portion of the oxide of zinc would require to be converted into slag; and this base being so ill adapted for the formation of slag, would prevent it from being of such a character as is required in the treatment with lead.

It may however happen that there are circumstances which would render the smelting of ore containing zinc blende in a reverberatory furnace advantageous and desirable; when, for instance, coal of good quality is to be had at a cheap rate, and the blast-apparatus for a shaft-furnace is not at hand, and then for the separation of the zinc recourse must be had to means which will serve as substitutes for those provided in the ordinary working of a shaft-furnace.

It would indeed be possible to effect the decomposition of the sulphide of zinc, and the volatilization of the zinc, in a reverberatory furnace, by mixing with the charge coal-dust or powdered coke; but this method would involve the application of such a very high temperature (perfect white-heat) as would only be attained by a considerable expenditure of time and fuel.

However, as it appeared that sulphuret of zinc is decomposed by metallic iron at a temperature which is somewhat less than that at which it is decomposed by carbon, and as oxide of iron in fine powder, in contact with carbon at a bright red heat is soon reduced by the carbonic oxide formed in the combustion and left in a pulverulent form, it was reasonable to suppose that when ore rich in zinc blende is to be melted in a reverberatory furnace, all that is requisite is, that the charge,—consisting of raw and well-roasted ore in proper proportions, together with the requisite quantity of coal-dust or coke-powder, and the fluxes suitable to produce the kind of slag needed,—should be melted at a sufficiently high temperature.

Some experiments made by the author on a small scale, both with ores containing pyrites and blende and with black zinc blende, gave the most satisfactory results. He obtained from the blende a matte quite as free from zinc as that from the pyritic ore, in all instances that the proportions of oxide of iron and coal adequate to the decomposition of the sulphuret of zinc were used.

If, for example, a pyritic ore to be smelted contains a considerable admixture of black zinc blende, which consists of $\text{FeS} + 3\text{ZnS}$ ($=23\text{FeS} + 77\text{ZnS}$), and contains 51.6 Zn with 25.4 S, and that it is wished to effect the decomposition in such a manner that the zinc may be removed in the state of vapour and the sulphur combined with iron to form FeS , then it will be necessary to have 44.4 iron in a metallic state, for FeS consists of 63.6 Fe and 36.4 S, and—

$$\frac{63.6 \times 25.4}{36.4} = 44.4.$$

Since this quantity of iron has to be liberated from oxide of iron formed in the roasting of the pyritic ore, and 44.4 Fe is combined with 19.0 O in oxide of iron, $63.4 \text{ Fe}^2 \text{ O}^3$ will be required, and about 7.1 carbon, for its reduction to the metallic state.

It must however be observed, that as all the oxide of iron is not

converted into metal, because two hours is the utmost time that can be bestowed upon the working of a reverberatory furnace, after which time the charge must be stirred, and further, as the coal used for reduction contains only a certain per-centage of carbon, it will be necessary for the decomposition of black zinc blende containing 77 per cent. of sulphide of zinc, to have at least 70 parts of oxide of iron and 9 or 10 parts of coal-dust or coke-powder.

As the heat in a reverberatory furnace must be communicated to the charge from the top to the bottom, it is possible that at many parts where the oxide of iron is not perfectly reduced, the heat may be sufficiently high for the direct decomposition of portions of the raw blende by the coal with which it is in contact. But even if this were the case, no sulphur would be lost, because the sulphide of carbon resulting from the decomposition and evolved in vapour, would react upon the oxide of iron and convert it into sulphide.

With regard to the formation of a suitable slag, the fluxes requisite will depend upon the nature of the earthy admixtures in the ore. The composition of the slag should be such, that with protoxide of iron, lime, and alumina chiefly for the basic constituents, it should correspond with the formula $m(\text{RO})^3 \cdot 2\text{SiO}^3 + n(\text{RO})^3 \cdot \text{SiO}^3 + \text{Al}^2\text{O}^3$, being at the same readily fusible, but not too liquid, so that the separation of the matte may take place with ease. The addition of slags rich in protoxide of iron, and consisting chiefly of monosilicates, such as the slags from the smelting with lead, or in their place an addition of well-roasted pyritic ore, will therefore be advantageous in most instances.

When there is a deficiency of alumina, an addition of siliceous clay is necessary; and when there is a deficiency of lime, either burnt lime, fluor spar, or both, may be added. The latter is especially desirable when the charge is rich in quartz, because in that case it produces a double effect, giving rise to the formation of fluoride of silicium, which escapes in vapour, while introducing lime into the slag, and serving moreover as a flux.

By ascertaining analytically the nature and proportion of the ingredients of the ore to be smelted, there is not much difficulty in calculating the quantity of substances requisite for the production of a slag suitable for the operation in a reverberatory furnace. Then by fusion-experiments on a small scale, at a temperature of about 1800° , the accuracy of the result thus obtained may be experimentally proved.

When it is necessary to provide the oxide of iron, for the decomposition of the sulphide of zinc and the production of a slag, by roasting ore containing pyrites and blende, this operation must be performed with the powdered ore in a reverberatory furnace, at a temperature raised gradually to 800° , and with a plentiful supply of air, so that all the sulphide of zinc may be perfectly oxidized. The oxide and sulphate of zinc formed at the same time do not, when there is a sufficiency of reducing substance, interfere with the attainment of the desired object; for the greater part of the oxide of zinc is reduced, partly by the action of the carbonaceous admixtures and

partly by the flame of the fuel, the zinc liberated escaping in vapour, while that of the sulphide of zinc resulting from the reduction in a similar manner of the sulphate of zinc is, for the most part, brought into a volatilizable state by reaction with the iron liberated from the oxide of iron, and serves to convert part of the oxide of zinc into slag. The smaller the amount of sulphate of zinc in such a roasted ore, the easier is the reduction of the oxide of zinc and the volatilization of the metal; and as the formation of a large proportion of sulphate of zinc in roasting pulverulent blende may be prevented by the application of a high temperature, attention must be paid to this point in the construction of the reverberatory furnace.

Lastly, it must be observed, that in roasting argentiferous blende, there is a somewhat greater loss of silver, in consequence of the high temperature required, than in roasting argentiferous pyritic ore free from blende; but the inconveniences attending the working of a matte rich in zinc are so great, and the loss of silver may be so much greater at a subsequent stage of the process, that the former must in most instances be regarded as unavoidable.—*Berg- und Hüttenm. Zeitung.*, 1854, No. 11.

On Madder Colours. By E. SCHWARTZ.

The author has investigated the behaviour of the colouring matter of madder towards fatty oils. The experiments made by him were as follows:—

1. He boiled madder flowers* with 8 to 10 times the quantity of poppy-oil, filtered it through flannel, and left the fluid to clear by standing. He then poured it into boiling water, containing pieces of stuffs which had been treated with a mordant; these gradually took the colour, and resisted brightening perfectly. [According to Schwartz, most of the colouring matter is extracted from madder by fatty oils; but Schæffer did not find this to be the case.]

2. Garancine, similarly treated, furnished a red fluid, which, when used as above with hot water and prepared stuffs, produced colours which resisted brightening better than those obtained with garancine in the ordinary way.

3. As in the second experiment, garancine was boiled in oil, and the whole (without filtration) brought into contact with the stuffs and the hot water; the colours did not resist brightening so well as in the previous experiment.

From the difference in the action of the fluid in the second and third experiments, the author concludes that garancine retains acids which acted injuriously on the drying process in No. 3, as the acids are only extracted from the fibrous substance by the contact of water with the thoroughly carbonized madder. M. Schæffer supports this opinion, that injurious remains of acids are retained in garancine, by an experiment in which he treated garancine with ammonia, and then employed it in dyeing, when it furnished better

* Prepared by boiling madder with acids, and fermenting.

results than were obtained with ordinary garancine.—*Bulletin de la Soc. Industrielle*, No. 122.

On the Advantages of the Twaddle's Areometer over those of Beaumé and Beck. By Dr. BOLLEY.

It appears very desirable to call the attention of chemists to Twaddle's areometer, not merely because the specific gravities of fluids heavier than water are always expressed in accordance with this instrument in the copious technical literature of England, but also because this areometer has great advantages over those in use on the continent, and deserves to take their place. In all the chemical factories of England which the writer had an opportunity of visiting, he became convinced that Twaddle's areometer fully deserved the estimation in which it is held by German and French manufacturing chemists who visit England, even though previously accustomed to Beaumé's.

The advantages of this instrument are,—1st, that for the distinction of the specific gravities between 1·000 and 2·000, it contains 200 degrees, so that it indicates much smaller differences in the density of fluids than Beaumé's areometer, which has only 76 degrees between 1·000 and 2·000 spec. grav. One bad result of such a more exact division would be the necessity of employing a very long scale, or having very small degrees; but both these disadvantages are to a certain extent avoided by making the entire apparatus consist of six areometers, of which the first ranges from 0° to 26°, the second from 24° to 60°, and so forth. The whole scale of degrees thus reaches a length of about 20 inches.

2. Each degree represents a *constant progression* of the specific gravity, so that, supposing we know the very simple principle of the division, on reading off the degree we immediately obtain the corresponding density of the fluids. The principle of this division is as follows:—The specific gravity of water being set at 1·000, every increase of density equal to 5 unities is represented by 1 degree; thus—

1° Twaddle	=1·005
2° ...	=1·010
7° ...	=1·035

The degree has consequently only to be multiplied by 5, and the number thus obtained added to 1·000, and we obtain the specific gravity of the fluid under examination.

Hence it follows that this areometer is one with a *rational* scale, and a further consequence is that the degrees must be of *unequal* length.

That the employment of this instrument would essentially simplify some calculations is evident from the following:—

1. A gallon (English) of distilled water weighs 10 lbs. (English). By sinking Twaddle's instrument into a solution, an acid, &c., and

multiplying the degree obtained by 5, we readily learn the weight of a gallon of the latter fluid. For instance, an acid of 50° Twaddle has the spec. grav. 1.250, and the gallon consequently weighs $12\frac{1}{2}$ lbs.; the gallon of another of 5° Twaddle weighs only $10\frac{1}{4}$ lbs.

2. With French measures and weights, the matter becomes still more simple; 1 litre of distilled water weighs 1000 grms; 1 litre of a fluid, say of 20° Twaddle, therefore weighs 1100 grms., *i. e.* $1000 + 20 \times 5$ grms.

3. If an acid or solution of a given degree is to be diluted to a lower strength, how much water must be employed. For instance, sulphuric acid of 170° Twaddle is to be diluted to 6°. The proportion for dilution is obtained by the division of 170 by 6; the quotient is 28.333; that is to say, when 1 litre of acid of 170° Twaddle is diluted to 28.333 litres, or in other words when 27.233 litres of water are added to it, we obtain a fluid of 6° Twaddle, for 170° Twaddle represents the spec. grav. 1.850 and 6° Twaddle, the spec. grav. 1.030, consequently the 28.333 litres contain 27.233 litres of water, and 1 litre of sulphuric acid weighing 1.850 grm.; the weight of the whole is $27.233 + 1.850$ grm. = 29.183 grms.; hence, by dividing the total weight, 29.183 grms., by the volume, 28.333 litres, we obtain the spec. grav. 1.030.

If it were desired to perform a similar calculation with the areometer of Beaumé or Beck, considerable errors would be induced.

From this it may readily be seen, that from an observation with Twaddle's areometer certain sound conclusions as to the nature of the fluid may be deduced; whilst Beaumé and Beck's instruments not only give imperfect and arbitrary results, but their indications do not stand in connexion with the nature of the substance under investigation.—*Schweiz. Gewerbebl.*, 1854, p. 33.

On the Occurrence of Cyanide of Potassium in the Melt obtained in the Manufacture of Ferrocyanide of Potassium. By A. REIMANN.

Liebig expressed the opinion that the yellow prussiate melt contains no ferrocyanide of potassium, but only cyanide of potassium. This opinion was contradicted by many chemists, especially by Gmelin and Runge. The author has examined various melts of this kind in Fresenius's laboratory; he finds that the melt whilst still hot contains no ferrocyanide of potassium. The ferrocyanide is only produced by the action of water or moist air upon the melt. The conversion of cyanide into ferrocyanide of potassium is facilitated by the presence of finely-divided amorphous sulphuret of iron and of caustic potash; sulphuret of iron which has become crystalline by exposure to too high a temperature has an unfavourable action. A temperature of 158°–176° F. is the best for the lixiviation.—*Journ. für Prakt. Chem.*, lx. p. 262.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Papaverine. By THOMAS ANDERSON, M.D.

IN the purification of narcotine by repeated crystallizations from boiling alcohol, the mother-liquors of each successive crystallization had been carefully preserved, and at the conclusion of the investigation of that substance, they were worked up for the purpose of obtaining the very considerable quantity of narcotine which they obviously still contained. For this purpose the fluids were mixed together, and the greater part of the alcohol separated by distillation. The residue, on being left to itself, deposited a considerable quantity of dark-coloured crystals mixed with resinous matters, which were collected on a cloth and expressed; and the fluid which passed through was again concentrated and allowed to crystallize, and this was repeated until it ceased to yield anything on further evaporation. The crystals so obtained were dissolved in the smallest possible quantity of boiling alcohol, from which they were deposited in a tolerably colourless state as the liquid cooled. On further concentrating this mother-liquor, and again allowing it to cool, it became filled with crystals of a substance obviously much more soluble in alcohol than narcotine, and differing from it in its general characters. It was particularly observed to restore the blue of reddened litmus, to dissolve readily in acids, and to saturate them completely—properties not possessed by narcotine. Its ready solubility in alcohol led at first to the suspicion that it might be thebaine, which had been already observed accompanying the narcotine; but the difference in its crystalline form, as well as its complete precipitation from its solution in acetic acid by subacetate of lead, proved it to be different. A very few experiments sufficed to show that the base thus obtained was still contaminated with narcotine, from which it might no doubt have been separated by repeated crystallizations; but as this would have been an extremely tedious process, and have caused the loss of a considerable quantity of material, I preferred a method founded on the marked difference between its basic properties and those of narcotine. The whole of the crystals obtained from the mother-liquors, and consisting partly of narcotine and partly of this other base, were reduced to a fine powder, and digested with a limited quantity of acetic acid. The acid was rapidly saturated, and as soon as the fluid had lost its acid reaction it was filtered from the undissolved portion, which was again treated with the acid; and

this treatment was cautiously repeated as long as it continued to be thoroughly saturated. The solution was then filtered from the undissolved narcotine, precipitated by ammonia, and the precipitate crystallized from boiling alcohol. The base was now pure, and analysis showed it to be papaverine, with which its characters were found to agree in all respects. A consideration of the properties of papaverine now enabled me to perceive that it must have been present in very large quantity in the mother-liquor obtained in the first crystallization of the crude narcotine, which had not been mixed with the others, but treated in a different manner for the preparation of thebaine, and it seemed probable that it would be found in abundance in the precipitate produced in that fluid by subacetate of lead. This opinion proved to be perfectly correct, and after a few trials it was found that it might be readily extracted in the following manner. The subacetate of lead precipitate was reduced to fine powder and boiled with alcohol, by which means a very dark fluid was obtained, which deposited a few crystals, apparently of narcotine, on cooling, and on further concentration a dark-coloured resinous substance was left. After the complete expulsion of the alcohol, the residual mass was treated with dilute hydrochloric acid, which dissolved narcotine and papaverine, and left a quantity of a black resinous matter, which was separated by filtration. The fluid was then concentrated and left to itself. In the course of a few days crystals of the sparingly-soluble hydrochlorate of papaverine began to make their appearance, and continued gradually to increase for some time. As soon as they ceased to increase, they were removed from the solution, which was found to contain narcotine, and purified by several crystallizations. The base was then separated by ammonia, and obtained in a state of absolute purity, by solution in boiling alcohol and crystallization.

Papaverine, as thus obtained, is in the form of minute radiated crystals, highly soluble in boiling alcohol; so much so that a saturated hot solution becomes nearly solid on cooling. It saturates the acids completely, and gives in the most distinct manner the reaction with strong sulphuric acid described by Merck*. Although the formula assigned to papaverine by its discoverer appeared to be correct, an analysis of that obtained by the process just described was made; and as, in the course of the investigation, it became necessary to ascertain by analysis whether particular specimens were free of narcotine, several additional combustions were obtained, the results of which are also given. The analyses were made with chromate of lead, the nitrogen determined by Peligot's method:—

	I.	II.	III.			
Carbon	70.71	70.60	70.58	40=240		70.79
Hydrogen	6.29	6.46	6.46	21	21	6.20
Nitrogen†	4.40	3.96	..	1	14	4.14
Oxygen	18.60	18.96	..	8	64	18.78

* Chem. Gaz., vol. vi. p. 309.

† Merck has published only one nitrogen determination of papaverine, giving 4.57 per cent., which greatly exceeds the calculated number. I have observed

These results correspond completely with the calculated numbers, and were sufficient to show that the base is papaverine; but for further security, a determination of the platinum in its platinum salt was made, when 5.684 grs. of the salt gave 1.013 gr. of platinum = 17.82 per. cent. Theory requires 18.10 per cent.

Action of Nitric Acid.

Papaverine dissolves in dilute nitric acid without decomposition, and with the formation of a nitrate; but if the solution be mixed with an excess of nitric acid, especially if concentrated, and heat be applied, a brisk action takes place, some red fumes are evolved, the fluid becomes dark red, and orange-coloured crystals begin to make their appearance, and gradually increase in quantity. Nothing can be simpler than the preparation of this substance. The degree of concentration of the acid is immaterial, for the product is sure to be obtained; and if the fluid be sufficiently concentrated, crystals begin to be formed the instant the heat is applied, and soon become so abundant as entirely to fill the fluid. If the solution be more dilute, they appear more slowly, and are then larger, more regularly formed, and much paler coloured. The only precaution necessary is, to avoid the use of too large an excess of nitric acid, as it dissolves the new product much more abundantly than water. The orange-coloured crystals are the nitrate of a new base, to which I give the name of nitropapaverine.

Nitropapaverine is readily obtained from its nitrate, by dissolving it in boiling water, and precipitating the hot solution by ammonia; but as the salt is very sparingly soluble even in hot water, it is more convenient to dissolve it in nitric acid, and then to add at once an excess of the alkali. A light yellow flocculent precipitate is immediately deposited, which is collected on a filter, dried, and dissolved in boiling alcohol, from which it is deposited on cooling. Nitropapaverine is thus obtained in pale buff-coloured needles, insoluble in water, but soluble in alcohol and æther. It restores the blue colour of reddened litmus, dissolves in the acids, neutralizes them completely, and forms a series of salts, all of which have a pale buff colour and are sparingly soluble in water. When heated, it undergoes fusion, and at a higher temperature it burns rapidly with a sort of deflagration. Concentrated solution of potash, when boiled with it, causes the evolution of traces of a volatile base. It does not give the purple reaction of papaverine with sulphuric acid. Its analysis gave the following results:—

Carbon	62.31	40 =	240	62.50
Hydrogen	5.21	20	20	5.20
Nitrogen	..	2	28	7.29
Oxygen	..	12	96	25.01

the same tendency to give an excess, having in one experiment obtained as much as 4.66. The only mode of explaining this anomaly was by supposing that the base carried down a small quantity of the ammonia which had been used to precipitate it. In order to ascertain whether this opinion was well founded, a quantity thrown down by potash was analysed, and the results are those of the second determination.

This corresponds closely with the calculated results for the formula $C^{40}H^{20}(NO^4)O^8$, which is further confirmed by the analysis of the platinum salt.

The crystals of the base deposited from alcohol contain 1 equiv. of water (2.29 per cent.), and have the formula $C^{40}H^{20}(NO^4)O^8 + HO$.

Nitrate of Nitropapaverine.—This salt is obtained by the action of nitric acid on papaverine, in the manner already described. It appears in the form of four-sided tables, sometimes of considerable size, and generally of a dark orange colour. By crystallization from boiling alcohol, it is got in a state of absolute purity, and then forms fine yellow crystals of great beauty. It is almost insoluble in cold water, but on boiling it is taken up in somewhat larger quantity, and deposited on cooling in an imperfectly-crystalline form. It is much more soluble in water containing nitric or hydrochloric acids, as well as in alcohol and æther. When gently heated, it melts, and then deflagrates, leaving a quantity of a nearly black substance, which burns away completely at a higher temperature. Potash and ammonia, when digested on it at ordinary temperatures, rapidly separate the base. The ease with which this substance is formed, and its extreme insolubility render its production a very useful reaction for papaverine, and by means of it I have succeeded in proving that this base also occurred in the fluid from which narcotine was separated by precipitation with ammonia. Nitrate of nitropapaverine is anhydrous. Its analysis gave,—

Carbon	53.68	40 =	240	53.69
Hydrogen	4.95	21	21	4.69
Nitrogen	..	3	42	9.38
Oxygen	..	18	144	32.24

corresponding with the formula $C^{40}H^{20}(NO^4)O^8 + HO NO^5$.

Hydrochlorate of Nitropapaverine is a sparingly soluble salt, crystallizing in pale yellow needles. It dissolves readily in spirit, and in excess of hydrochloric acid.

Sulphate of Nitropapaverine is but little soluble in water. It crystallizes in minute prisms.

Platinochloride of Nitropapaverine is thrown down as a pale yellow precipitate, when bichloride of platinum is added to a solution of the hydrochlorate. Its analysis gave the following results,—

Carbon	40.47	40 =	240	40.66
Hydrogen	3.80	21	21	3.55
Nitrogen	..	2	28	4.72
Oxygen	..	12	96	16.26
Chlorine	..	3	106.5	18.09
Platinum	16.56	1	98.7	16.72

corresponding with the formula $C^{40}H^{20}(NO^4)O^8 HCl + PtCl$.

The rest of the salts of nitropapaverine have not been minutely examined.

Action of Bromine on Papaverine.

When bromine-water is added, drop by drop, to a solution of hydrochlorate of papaverine, a precipitate is obtained, which at first immediately redissolves, but on the further addition of bromine-water at length becomes permanent. It is the hydrobromate of a derivative base, bromopapaverine.

Bromopapaverine itself is easily obtained from this substance, by digesting it with ammonia, and dissolving the product in boiling alcohol. It is deposited on cooling in minute white needles, insoluble in water, but readily soluble both in alcohol and æther. It dissolves in the acids and forms salts, the greater number of which are characterized by their sparing solubility. Its crystals were anhydrous, and gave on analysis numbers leading to the formula $C^{40}H^{20}BrNO^8$:—

Carbon	57.23	40 =	240	57.41
Hydrogen	5.02	20	20	4.78
Nitrogen	..	1	14	3.34
Oxygen	..	8	64	15.34
Bromine	19.45	1	80	19.13

Hydrobromate of Bromopapaverine.—This salt is obtained, as already mentioned, by the addition of bromine-water to a solution of hydrochlorate of papaverine. It varies somewhat in its appearance, according to the degree of concentration of the solution from which it is obtained. If concentrated, it is deposited with a more or less yellow colour, and is apt to form resinous lumps, particularly if the bromine-water is added rapidly; but when the solutions are more dilute, it appears in the form of a perfectly white powder. It is well washed with water, dissolved in boiling spirit, and on cooling is deposited in a state of purity in the form of a crystalline powder, insoluble in water, and sparingly soluble in alcohol. When gently heated, it melts, and is decomposed. When digested with potash or ammonia, it is decomposed, with separation of the base. Its crystals are anhydrous, and gave on analysis,—

Carbon	48.36	40 =	240	48.09
Hydrogen	4.35	21	21	4.20
Nitrogen	..	1	14	2.80
Oxygen	..	8	64	12.85
Bromine	32.48	2	160	32.06

corresponding with the formula $C^{40}H^{20}BrNO^8 + HBr$.

Hydrochlorate of Bromopapaverine is soluble in water, though sparingly. The rest of its salts have not been examined.

Action of Chlorine on Papaverine.

When a current of chlorine is passed through a solution of hydrochlorate of papaverine, the fluid becomes brown, and after a time a dirty gray precipitate makes its appearance, which is insoluble, or nearly so, in water, but dissolves in boiling alcohol, and gives a resinous deposit as the solution cools. When treated with ammonia,

hydrochloric acid is separated, and a powder is obtained which is obviously a chlorine base. It dissolves in the acids, and is reprecipitated by ammonia. Alcohol takes it up, and deposits it in an amorphous form on cooling or by spontaneous evaporation. The properties of this substance proving unsatisfactory, I then tried the action of chlorate of potash added in small successive portions to a solution of papaverine in excess of hydrochloric acid, but the same amorphous gray powder being produced, I did not pursue the subject further; for although one or more derivative bases are unquestionably produced, their properties are not sufficiently well marked to admit of their proper purification.

Action of Iodine on Papaverine.

When an alcoholic solution of papaverine is mixed with tincture of iodine, and the solution is left to itself for some hours, small crystals are slowly deposited; and by further evaporation of the fluid from which they have been removed, another substance is obtained.

Teriodide of Papaverine.—To the crystals first separated I give this name. They are purified by solution in boiling alcohol, from which they are slowly deposited in small rectangular prisms. Their colour is purple by reflected, and dark red by transmitted light. They are insoluble in water, but soluble in alcohol. It is not acted upon by dilute acids, but ammonia and potash rapidly decompose it, removing iodine and leaving papaverine. From this fact it is clear that it is not the salt of a substitution base, but corresponds in constitution with the teriodide of codeine, which I described in a former paper*. Analysis gave,—

Carbon	33.02	40 =	240	33.47
Hydrogen.....	3.21	21	21	2.92
Nitrogen	..	1	14	1.95
Oxygen	..	8	64	8.95
Iodine	52.90	3	378	52.71

The formula of the substance is therefore $C^{40}H^{21}NO^8 + I^3$.

Pentiodide of Papaverine.—By evaporating the mother-liquor of the teriodide, this compound is deposited, and is purified from excess of iodine by crystallization from alcohol. It then forms slender needles, with an orange colour by transmitted light and a reddish-bronze surface colour. It is much more soluble in alcohol than the teriodide, but is insoluble in water. It loses iodine by the application of a moderate heat, although perfectly stable at 212° . It is insoluble in acids, and is rapidly decomposed by ammonia. Its composition was,—

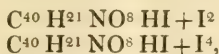
Carbon	24.78	40 =	240	24.76
Hydrogen	2.59	21	21	2.16
Nitrogen	..	1	14	1.44
Oxygen	..	8	64	6.63
Iodine	64.60	5	630	65.01

These results give the formula $C^{40}H^{21}NO^8 + I^5$.

It is difficult to form a rational conception of the constitution of

* Edinburgh New Philosophical Journal, vol. i. p. 103.

these substances. The formulæ given above seem to be on the whole the most probable; but it is clear that the analyses admit of a different interpretation, and we may assume these compounds to be hydriodates with excess of iodine, and represent their constitution by the formulæ—



the additional atom of hydrogen making too small a difference to be important. We have however no experiments to enable us to decide between these two views, which could only be done by an extended investigation of the similar compounds of the other bases; and in the absence of further information, I have chosen to represent them as iodides, simply because it involves less hypothesis, and sufficiently expresses their constitution.

Action of Soda Lime on Papaverine.

Papaverine was mixed with about four times its weight of a soda lime, composed of equal weights of its constituents, and the mixture heated in the oil-bath. At 250° traces of a volatile base began to appear, which increased in abundance when the temperature rose to 300°. After the heat had been continued for some hours, a small quantity of a pungent base was collected in the receiver. It gave white fumes with hydrochloric acid, and with bichloride of platinum a highly soluble salt, precipitated by alcohol and æther in shining plates. A determination of the platinum in this compound gave 36·21 per cent., which lies almost exactly between the numbers required for propylamine and æthylamine, the calculated number for the former being 37·21, for the latter 35·34. It is probable that the substance analysed actually contained both bases, but from the small scale on which it was necessary for me to work, I was precluded from any attempts to substantiate this opinion.—*Transactions of the Royal Society of Edinburgh*, vol. xxi. part 1.

On the Formation of Æther. By ALVARO REYNOSO.

In opposition to the views recently put forward upon the theory of the formation of æthers by Williamson, Chancel and Berthelot, the author refers to the remarkable production of æther in the presence of a body which itself undergoes no change. Such a body is iodide of mercury.

Iodide of mercury, prepared by precipitation, was put with absolute alcohol into a glass tube, which was then closed by fusion. It was then heated to 572° F. in a gun-barrel. At this temperature the alcohol is decomposed, and the mass becomes black. When this has taken place, the tube must be thrown away as far as possible to smash it to pieces, as breaking it is very dangerous. But if it be heated only to 464° F. for four or five hours, the iodide remains crystallized, a portion of it is dissolved, the salt is not decomposed, but a considerable quantity of æther is formed.—*Comptes Rendus*, vol. xxxix. p. 696.

On the Chinese Yellow Berries. By M. VON ORTH.

The author has examined the dye-stuff which has been recently imported under the name of "Chinese yellow berries," and which has already been made the subject of an investigation by Professor Stein of Dresden*. Its value in dyeing has also been tested by Von Kurrer.

The fruits were pounded, and extracted with alcohol as long as the fresh portions added acquired a distinct yellow colour. The alcoholic extracts were mixed, and concentrated by the water-bath in a retort with an atmosphere of carbonic acid. On cooling, and especially on the addition of water, a small quantity of a fluid fat separates; this was separated from the fluid by means of a wet filter. The solution thus purified, which was of a fine reddish-yellow colour, was mixed with solution of acetate of lead, which produced a yellow precipitate. This was decomposed under water by sulphuretted hydrogen, and the fluid filtered from the sulphuret of lead, which retained the greater portion of the colouring matter, and was preserved in order to obtain this from it. The filtrate was again precipitated with acetate of lead, and the precipitate decomposed by sulphuretted hydrogen. The new portion of sulphuret of lead retains the remainder of the colouring matter; the fluid contains the tannic acid, which produces a green colour with salts of iron. By evaporating its pale yellow watery solution in an atmosphere of carbonic acid, and drying the residue *in vacuo*, an amorphous brownish-yellow mass was obtained, the analysis of which gave—

Carbon	47.47	46 =	276	47.26
Hydrogen	6.22	36	36	6.16
Oxygen	46.31	54	272	46.58

A portion of the solution of the tannic acid was heated, and precipitated with tribasic acetate of lead; the precipitate, which was of a yellow colour with a grayish-green tinge, was washed with water, and dried at 212° F. Its analysis gave—

Carbon	22.89	46 =	276	23.3
Hydrogen	2.34	28	28	2.3
Oxygen	17.38	26	208	17.7
Oxide of lead	57.39	6	670.428	56.7

After deducting the oxide of lead, its composition is as follows:—

Carbon	53.71	46 =	276	53.91
Hydrogen	5.50	28	28	5.47
Oxygen	49.79	26	208	49.62

The acid dried *in vacuo* therefore contains 8 eqivs. of water:—
 $C^{46}H^{28}O^{26} + 8HO = C^{46}H^{36}O^{34}$. The fluid, deprived of its tannic acid and colouring matter by solution of acetate of lead, and heated with muriatic acid, furnished first of all a slight brown precipitate, which was removed by filtration, and afterwards, when heated to boiling, gave flakes of a dark green body, which presented the closest similarity in all its properties to the green product of decomposition

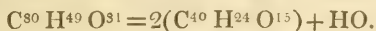
* See Chem. Gaz., June 15, 1853, p. 221.

produced by the action of acids upon the rubichloric acid of the *Stellata*. Its composition also is exactly similar. It was washed with water, dried *in vacuo*, and then analysed. The results were,—

Carbon	74.82	48 =	288	74.81
Hydrogen	6.46	25	25	6.49
Oxygen	18.72	9	72	18.70

The entire quantity of sulphuret of lead obtained in the manner above described was extracted with alcohol of spec. grav. 0.828, the solution filtered whilst hot, and evaporated to one-fourth of its volume in a current of carbonic acid gas on the water-bath. The residue was then brought to the consistence of a syrup over sulphuric acid *in vacuo*. This mass, which was of the colour of bichromate of potash, was repeatedly agitated with æther as long as the latter acquired a yellow colour. The æther was evaporated, and the residue treated with water. The reddish-yellow residue, which was insoluble in water, was dried at 212° F., and analysed. The quantity of this resinous colouring matter is extremely small. Its analysis gave—

Carbon	61.55	80 =	480	61.78
Hydrogen	6.66	49	49	6.31
Oxygen	31.79	31	248	31.91



The portion of the colouring matter which was insoluble in æther furnishes a very small quantity of a yellow colouring matter to absorb alcohol; this however was not obtained in sufficient quantity to render an analysis or any further examination of it possible. The portion insoluble in alcohol constitutes the great mass of the colouring matter, although even its amount is inconsiderable when compared with the quantity of fruit. It contains a large amount of incombustible constituents, which appeared to be lime with a little oxide of iron. The quantity of this body was too small to allow of any experiments to free it from these mineral constituents. When dried at 212°, it formed an amorphous mass of a fine yellow colour, insoluble in alcohol and æther. Analysis:—

Carbon	50.57	40 =	240	50.63
Hydrogen	7.35	34	34	7.17
Oxygen	42.08	25	200	42.20



The yellow berries, which had been exhausted by alcohol, were extracted with water, and the decoction concentrated by evaporation. On the addition of alcohol, a gelatinous mass separates; this was separated from the alcoholic fluid by means of a linen filter. The mother-liquor was got rid of, as far as possible, by pressing between linen; the jelly was then dissolved in water, mixed with animal charcoal, and boiled. The solution of the jelly filtered from the animal charcoal was mixed with muriatic acid, and the jelly was then again thrown down by alcohol. The flakes separated would

soon clog the filter if the fluid in which they are suspended is not heated; by this means they become less voluminous, and the filtration goes on more rapidly. They are washed with alcohol until no trace of muriatic acid is contained in the fluid as it runs away, then pressed between linen, and dried in the water-bath. Dried at 212° F. and analysed, this substance gave,—

Carbon	42.04	32 =	192	42.10
Hydrogen	5.36	24	24	5.26
Oxygen	52.60	30	240	52.64

$C^{32} H^{34} O^{30}$ or $C^{64} H^{48} O^{60}$ is distinguished from pectine ($=C^{64} H^{48} O^{64}$ according to Fremy) by a somewhat smaller amount of oxygen. The alcoholic mother-liquor, from which the jelly had been deposited, was precipitated by a solution of acetate of lead, and filtered from the precipitate; water with a little acetic acid was then poured over the latter. The acid solution was filtered away, the lead removed by sulphuretted hydrogen, and the solution of tannic acid separated from the sulphuret of lead concentrated on the water-bath; the residue, dried at 212° F., gave on analysis,—

	I.	II.		
Carbon	52.73	52.62	46 =	276 52.28
Hydrogen	5.75	5.86	29	29 5.56
Oxygen	41.52	41.52	27	216 41.46

$C^{46} H^{29} O^{27} = C^{46} H^{28} O^{26} + HO$. $C^{46} H^{28} O^{26}$ is the composition of the acid combined with oxide of lead.

The anhydrous tannic acid is therefore $=C^{46} H^{28} O^{26}$.

The hydrated tannic acid $=C^{46} H^{28} O^{26} + HO$.

The acid dried *in vacuo* $=C^{46} H^{28} O^{26} + HO + 7Aq$.

The small quantity of substance did not permit of any inquiry as to whether this acid was a conjugate carbohydrate. It is homologous with æsculine, $C^{42} H^{24} O^{26} + 4CH = C^{46} H^{28} O^{26}$.—*Sitzungsbericht der Akad. der Wiss. zu Wien*, xiii. p. 590.

On the Water of Crystallization in some Double Salts.

By H. ROSE.

A double salt of sulphate of lime and sulphate of potash, analogous in its composition to polyhalite, was observed by A. Phillips in a tartaric acid factory in London, forming beautiful tabular crystals. Its composition accords with the formula $KO SO^3 + CaO SO^3 + HO$, and it appears probable that the same agreement occurs between the forms of these two substances as between their compositions. This double salt may easily be prepared artificially; but in this case it is not obtained in distinct crystals, but in the form of a silky, paper-like mass.

If this double salt be heated, and deprived of its water of crystallization, it becomes, like polyhalite, far more readily decomposable by water than in its original state. Nevertheless the result of the experiments may often appear to be quite different, as after ex-

posure to a certain heat, the sulphate of lime is left of such a voluminous consistency when treated with water, that only a small quantity of the solution can be separated from it. This is not the case with the salt before it is heated; and as, when this is treated with water, the sulphate of lime retains a much smaller volume, the separated solution often contains more of the soluble salt than when the double salt has been heated.

The author has also succeeded in preparing an artificial crystalline compound of sulphate of strontia and sulphate of potash. It consists of equivalents of the two salts. He did not however succeed in preparing artificially the compound of sulphate of lime with sulphate of soda, which exists in nature as glauberite. Glauberite contains no water of crystallization; it consequently exhibits the same behaviour when treated with water, either before or after heating.

On few double salts is the influence of water so different before and after exposure to heat, as on Gaylussite, or the compound of carbonate of lime and carbonate of soda with water of crystallization. If the double compound be deprived of its water of crystallization, which may be easily and completely driven off at 212° F., it behaves like a mixture of carbonates of lime and soda, and water then separates the two constituents so completely, that a quantitative analysis might be effected in this way, whilst the unheated compound is but slowly and gradually decomposed by water.—*Bericht der Akad. der Wiss. zu Berlin*, 1854, p. 523.

On Æthal. By Prof. HEINTZ.

The product of the saponification of spermaceti consists principally of bodies analogous in their composition to alcohol, that is to say, its constituents all agree in composition with the formula $C^n H^{n+2} O^2$. It was formerly supposed that this was a pure substance, consisting of $C^{32} H^{34} O^2$. The author however had long since ascertained that the body obtained by the repeated recrystallization of crude æthal from alcohol is a mixture of two substances, which he distinguished by the names of stethal ($C^{36} H^{38} O^2$) and æthal ($C^{32} H^{34} O^2$). In examining the substance remaining dissolved in alcohol in this recrystallization, the presence of these two bodies was also ascertained. But this also contains other substances, which, although they could not be prepared in a state of purity, were nevertheless proved to exist as certainly as stethal and æthal, neither of which have been obtained chemically pure. To bring these bodies into such a form as would enable them to be more easily separated, the mass remaining after the evaporation of the alcohol was mixed with an excess of potash lime, and exposed to a constant heat of 518° – 527° F. in a metal bath until the evolution of hydrogen, which at first is very strong, had entirely ceased. The elevation of the temperature to 536° F. caused evolution of gas to recommence. The fatty acid separated from the mass by boiling with dilute muriatic acid, was perfectly free from any trace

of undecomposed æthal; the author ascertained this fact by means of the method formerly described by him for the separation of the fatty acids, when it proved to be a mixture of the same four acids produced with æthal by the saponification of spermaceti, namely, stearic, palmitic, myristic and laurostearic acids. As the action of the potash lime upon the æthal had produced nothing but the fatty acids and hydrogen, the only decomposition that takes place must be as follows:—The potash salts of the four anhydrous acids $C^n H^{n-1} O^3$ have been formed from the corresponding alcohols, which contain the same number of atoms of carbon, with evolution of $4H$, arising partly from the alcohol $C^n H^{n+2} O^2$, and partly from the hydrate-water of the hydrate of potash.

From this we may form some idea of the composition of the æthal examined. This must have been composed of the alcohols corresponding with stearic, palmitic, myristic, and laurostearic acids, which the author denominates *stethal*, *æthal*, *methal* and *lethal*. The composition of the two first has been given above; methal consists of $C^{28} H^{30} O^2$, and lethal of $C^{24} H^{26} O^2$. To the radicals contained in these four alcohols the author gives the names of *stethalyle* ($C^{36} H^{37}$), *æthalyle* ($C^{32} H^{33}$), *methalyle* ($C^{28} H^{29}$), and *lethalyle* ($C^{24} H^{25}$). Spermaceti, therefore, if each of the acids produced by its saponification be combined with each of these radicals, will consist of sixteen differently constituted æthers. But if we suppose that each acid is only combined with the oxide of the radical containing an equal number of equivalents of carbon, the substance will consist of—

Stearate of oxide of stethalyle	$C^{36} H^{35} O^3 + C^{36} H^{37} O$,
Palmitate of oxide of æthalyle	$C^{32} H^{31} O^3 + C^{32} H^{33} O$,
Myristate of oxide of methalyle . .	$C^{28} H^{27} O^3 + C^{28} H^{29} O$, and
Laurostearate of oxide of lethalyle	$C^{24} H^{23} O^3 + C^{24} H^{25} O$.

Monatsber. der Akad. der Wiss. zu Berlin, 1854, p. 562.

On some new Compounds of Lactic Acid. By A. STRECKER.

The author has obtained the following salts in the endeavour to obtain a crystallizable and readily fusible lactate, which might serve for the preparation of lactic æther. These salts, as they contain two different metallic oxides, speak strongly in favour of Gerhardt's opinion, that lactic acid is bibasic.

Lactate of Potash and Lime, $CaO, KO, C^{12} H^{10} O^{10}$.—This salt is obtained by dividing a solution of lactate of lime into two equal parts, precipitating one of these by carbonate of potash, mixing the clear solution with the other portion, and evaporating on the water-bath. The syrupous residue dries in the form of transparent grains. When the carbonate of potash is in excess, the grains are larger; but in this case a portion of the salt does not crystallize. The grains are quickly washed with water, when the crystals appear to be monoclinometric octahedra. They dissolve slowly in water, but readily when the water is hot; on cooling, lactate of lime crystal-

lizes from the solution. At 248° F. the crystals lose nothing in weight; they fuse at a higher temperature without decomposition, and solidify on cooling into a glassy mass. Analysis of the salt, dried at 248° F.:—

$C^{12}H^{10}O^{10}$	68.4	68.2	1 =	162.0	68.3
CaO	11.2	11.3	1	28.0	11.8
KO	20.4	20.5	1	47.1	19.9

Lactate of Soda and Lime, CaO , NaO , $C^{12}H^{10}O^{10} + 2HO$, is obtained in the same way as the preceding salt; it crystallizes from the concentrated solution on cooling, in colourless, transparent, hard grains, which lose water and become opake when heated to 212° F., and fuse at a higher temperature. Analysis of the salt dried over sulphuric acid:—loss of water = 7.8 per cent. at 266° F. The dry salt gave,—

$C^{12}H^{10}O^{10}$	73.6	1 =	162	73.3
CaO	12.6	1	28	12.7
NaO	13.8	1	31	14.0

Lactate of Soda and Oxide of Zinc, ZnO , NaO , $C^{12}H^{10}O^{10} + 2HO$.—The solution of lactate of zinc is partially precipitated with carbonate of soda, and the solution evaporated on the water-bath. The syrupous residue furnished a crystalline mass, which, when dried over hydrated sulphuric acid, dissolved readily in water. Oxide of zinc crystallized from the solution when moderately diluted. The crystals, dried at the ordinary temperature over sulphuric acid, lost 9 per cent. of water when heated to 248° F. (1.917 gram. lost 0.1775 gram.). The analysis of the salt, dried at 248° F., gave,—

$C^{12}H^{10}O^{10}$	..	1 =	162.0	69.4
ZnO	17.2	1	40.5	17.3
NaO	..	1	31.0	13.3

Lactate of Potash and Oxide of Zinc, prepared in the same way as the preceding salt, contained no water of crystallization when dried over sulphuric acid.

Lactate of Oxide of Æthyle, $2C^4H^5O$, $C^{12}H^{10}O^{10}$.—The preparation of this æther has already been attempted by Lepage. If 1 part of dry lactate of potash be mixed with 1.4 part of sulphovinate of potash, and the whole heated in a retort, the action commences about 292° F. When further heated, without passing the temperature of 356° F., the decomposition of the substances is completed.

The distillate which passes over during this operation has an unpleasant persistent odour, which probably arises from a small quantity of some body containing sulphur. When brought into contact with fused chloride of calcium, it dissolves it in abundance with evolution of heat, and the mass soon afterwards solidifies almost completely, forming an aggregation of transparent, colourless, crystalline grains, which appear to be rectangular prisms. The crystals fuse when heated, and then evolve vapours which are readily condensable, whilst a residue of colourless chloride of calcium is left.

These crystals have the composition $\text{CaCl} + 2\text{C}^4 \text{H}^5 \text{O}$, $\text{C}^{12} \text{H}^{10} \text{O}^{10}$. Their analysis gave,—

	I.	II.	III.			
C	40.4	..	40.8	20 =	120	41.2
H	6.8	..	6.8	20	20	6.9
O	..	..	..	12	96	32.8
Cl	19.2	{ 12.9 }	19.2	{ 1	35.5	12.2
Ca				{ 1	20	6.9

If these crystals be heated in a retort, pure lactate of oxide of æthyle is obtained. The distillate is a colourless fluid of a faint odour; its specific gravity is 1.08, and it possesses no constant boiling-point. It distils over principally between 292° and 310°F ., mixes with water, alcohol, and æther in all proportions, and has no reaction upon vegetable colours. When mixed with water, however, it immediately exhibits an acid reaction. When this mixture is boiled with oxide of zinc, lactate of zinc crystallizes from the solution on cooling.

Hence it appears that lactic æther, when decomposed by water, does not produce any æthylolactic acid, but gives rise to lactic acid and alcohol. When lactic æther is mixed with absolute alcohol, and dry ammonia is passed into the mixture, lactamide is produced, which remains in colourless laminar crystals when the solution is evaporated. The results of the determinations of the density of the vapour of lactic acid gave 4.75. 20 vols. C, 40 vols. H, 12 vols. O = 32.62, give 4.08 when divided by 8.

The vapour consequently occupied 8 vols., so that to arrive at the usual proportion of 4 vols., the above formula must be divided by two = $\text{C}^4 \text{H}^5 \text{O}$, $\text{C}^6 \text{H}^5 \text{O}^5$. The author here refers to the existence of monobasic lactic acid (lactic acid from flesh), and thinks that the anomaly may perhaps be explained by a conversion of the ordinary lactic acid into the latter; he nevertheless puts off the decision of this question for further investigation.

Benzolactic Acid, $\text{HO}, \text{C}^{20} \text{H}^9 \text{O}^7$.—The author has recently re-examined this acid, referred to in the investigation of benzoglycollic acid published by himself and Socoloff.

To prepare benzolactic acid, a mixture of 10 parts of syrupous lactic acid with 14 parts of benzoic acid is heated by means of a bath to 292°F . in a retort. Water distils over, and the neck of the retort contains benzoic acid. If a temperature of 392°F . is then kept up for some hours, the retort contains a fused mass of a pale brown colour, which on cooling solidifies very slowly into a mass of crystals. This is always a mixture of benzoic and benzolactic acids. If this be boiled with a solution of a quantity of carbonate of soda not sufficient for its complete saturation, the benzolactic acid, as the strongest acid, combines first with the soda, and the benzoic acid as well as the coloured matter remains principally in the residue. The watery solution then contains no more benzoic acid than is soluble in water, and this small quantity may easily be extracted from the fluid by shaking it with æther. The addition of muriatic acid then

separates colourless crystals of benzolactic acid from the watery solution; these are purified by recrystallization from water, or æther and alcohol.

The crystals of benzolactic acid are sometimes laminar, sometimes lanceolate; they feel rather fatty, and fuse when dry at 233°F . On cooling, the acid remains fluid, and only solidifies into a crystalline mass after a considerable time. It does not sublime when heated to 212° or 248°F . When strongly heated, it boils, and crystals, apparently of unaltered acid, are sublimed. The acid is soluble in 400 parts of cold water, but dissolves more readily in boiling water.

When boiled with water, it is slowly decomposed, forming lactic and benzoic acids. When boiled for twelve hours with diluted sulphuric acid, benzoic acid and ordinary lactic acid were obtained.

When boiled with a quantity of water not sufficient for its solution, the undissolved portion of the acid melts. The air-dried acid loses no water at 212°F . Its analysis gave,—

C	61.6	20 = 120	61.8
H	5.2	10 10	5.2
O	33.2	8 64	33.0

The *soda salt* obtained by saturation with carbonate of soda, evaporation and extraction with alcohol, forms shining crystals.

Benzolactate of Baryta, $\text{C}^{20}\text{H}^9\text{O}^7$, BaO , forms thin, shining, six-sided laminæ. The air-dried salt lost 17.6 per cent. of water at 212°F . (0.4570 grm. lost 0.0802 grm.), representing 6 equivs. of water (calculated 17.1 per cent.). The salt, dried at 212°F , gave,—

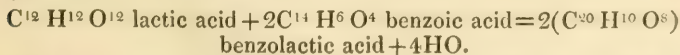
$\text{C}^{20}\text{H}^9\text{O}^7$	70.9	185.0	70.7
BaO	29.1	76.5	29.3

Benzolactate of Silver, $\text{C}^{20}\text{H}^9\text{O}^7$, AgO , is obtained by mixing nitrate of silver with a solution of benzolactic acid in ammonia, in the form of a flocculent precipitate; it dissolves in boiling water, and forms fine colourless needles on cooling. Analysis:—

$\text{C}^{20}\text{H}^9\text{O}^7$	63.9	1 = 193	64.5
AgO	36.1	1 108	35.5

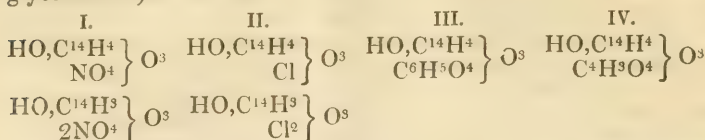
Neutral solutions of the salts of benzolactic acid are not precipitated by acetate of lead. By the addition of ammonia a precipitate makes its appearance, but only after a considerable time.

From the preceding statements, it appears that the formation and decomposition of benzolactic acid may be expressed by the following equation:—

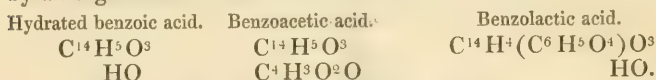


The author regards the acid as monobasic. With regard to its constitution, the following consideration renders it probable that it may be a conjugate compound of benzoic acid with lactide, $\text{C}^6\text{H}^4\text{O}^4$. The author considers that, as benzolactic acid has just as much resemblance to benzoic acid as nitrobenzoic and chlorobenzoic acids,

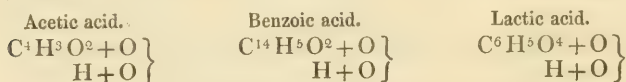
the formulæ of benzolactic and benzoglycolic acids may be expressed in the same way as those of the two former acids, as follows (I. nitrobenzoic acid, II. chlorobenzoic acid, III. benzolactic acid, IV. benzoglycolic acid):—



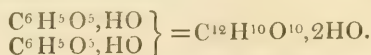
These acids are consequently distinguished from the compounds of benzoic acid with acetic and similar acids discovered by Gerhardt, by the circumstance that in the latter the hydrogen of the hydrate water is displaced by an organic radical, whilst in benzolactic acid a portion of the hydrogen in the radical of benzoic acid is replaced by an organic radical:—



The author consequently supposes the existence of a radical *lactyle*, of the formula $\text{C}^6\text{H}^5\text{O}^4$, in benzolactic acid; this stands in the same relation to lactic acid (regarded as a monobasic acid) as Gerhardt's acetylene, $\text{C}^4\text{H}^3\text{O}^2$, to acetic acid, or Liebig's benzoylene, $\text{C}^{14}\text{H}^5\text{O}^2$, to benzoic acid:—



Lastly, to make the formation, decomposition, and density of vapour of lactic acid, which correspond better with a monobasic acid, agree with the formula of lactic acid, $\text{C}^{12}\text{H}^{10}\text{O}^{10}$, 2HO , as a bibasic acid, the author supposes that the atom of lactic acid consists of two similar groups, which separate under certain circumstances, but recombine under other conditions:—



The lactic acid from flesh is perhaps one of the atomic groups contained in the ordinary lactic acid.—Liebig's *Annalen*, xci. p. 352.

On Cuminic Alcohol. By Dr. C. KRAUT.

According to Gerhardt and Cahours, Roman oil of cumin is a mixture of two substances,—cuminic aldehyde, or hydruret of cumyle, homologous with oil of bitter almonds, or hydruret of benzoylene, and cymene, a carbohydrogen.

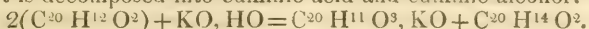
With melting potash this oil is converted into cuminate of potash, and with a solution of potash it forms several bodies, which have been observed by Gerhardt and Cahours, but not minutely studied.

The Roman oil of cumin was distilled until it was separated into

two portions, one of which, boiling at 190°C ., contained the greater part of the cymene; and the other, containing the cuminic aldehyde, did not boil at 200°C .

The cuminic aldehyde was mixed with a concentrated solution of bisulphite of soda. The mixture became warm, and solidified to a crystalline mass. This was pressed between blotting-paper, to free it from the mother-liquor and any adhering cymene. On mixing this with a solution of potash, and distilling with water, the cuminic aldehyde was obtained pure.

By acting on cuminic aldehyde with an alcoholic solution of potash, it is decomposed into cuminic acid and cuminic alcohol:—



2 parts of a saturated alcoholic solution of potash were mixed in a flask with 1 part of cuminic aldehyde, and so connected with a Liebig's condenser, that when boiled the vapours should condense and fall back into the flask. The mixture was boiled in this way an hour, then diluted with 12 times its bulk of water, and distilled. A quantity of alcohol distils over containing much of the cuminic alcohol dissolved, which on the addition of water floats on the surface as a clear liquid.

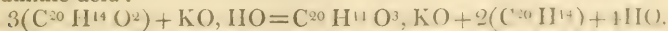
This cuminic alcohol was treated with bisulphite of potash, to separate any adhering cuminole, washed with water, and after drying over chloride of calcium, distilled. It began to boil between 170°C . and 180°C ., at which temperature some quantity passed over; the mercury then rose rapidly to between 240° and 250°C ., and remained tolerably constant till near the end of the distillation.

The first portion of the distillate contains some cymene, the result of a secondary action of the potash on the cuminic alcohol, which it is impossible entirely to avoid.

A portion of the liquid boiling at 243°C . was used for analysis. The formula $\text{C}^{20}\text{H}^{14}\text{O}^2$ requires 80.00 per cent. carbon and 9.33 per cent. hydrogen. The mean of four analyses gave 79.56 per cent. carbon and 9.36 per cent. hydrogen.

Cuminic alcohol is a clear oily liquid, of weak, pleasantly aromatic smell, and burning spicy taste; boils at 243°C . without decomposition, and is unaltered when exposed for a long time to the air. It is soluble in æther and alcohol, insoluble in water, and forms no compound with alkaline bisulphite. Warmed with potassium, it forms, under evolution of hydrogen, a yellow granular mass, which is decomposed by water into cuminic alcohol and potash. By nitric acid it is converted into cuminic acid. With concentrated sulphuric acid it forms no conjugate acid. When warmed with chloride of benzoyle, it forms a butyraceous, indistinctly crystalline mass, which has probably the formula $\text{C}^{20}\text{H}^{13}\text{O}, \text{C}^{14}\text{H}^5\text{O}^3$.

Cuminic alcohol, by long-continued boiling with 6 times its volume of a saturated solution of potash, is converted into cymene and cuminic acid:—



This reaction is not dependent on the presence of alcohol, for it takes place when cuminic alcohol is boiled with solid potash.

From the cymene obtained in these experiments, dinitrocymene was prepared. Cymene was carefully dropped into a mixture of concentrated sulphuric and fuming nitric acids, warmed to about $50^{\circ}\text{C}.$, and allowed to stand two days. When the mixture was diluted with water, a brown liquid body separated, which on standing became solid and crystalline. This was dissolved in boiling alcohol; on cooling, some uncrystallizable bodies separated; and on evaporation, dinitrocymene crystallized out in colourless, beautifully iridescent, rhombic tables. These melt at $54^{\circ}\text{C}.$, are soluble in æther and alcohol, but not in water. When heated, they detonate, and leave a very difficultly combustible charcoal.

Two analyses gave results agreeing with the formula $\text{C}^{20}\text{H}^{12}\text{2NO}^4$.
—*Ann. der Chem. und Pharm.*, vol. xcii.

PATENT.

Patent granted to Henry Bernoulli Barlow, for Improvements in Waterproofing Textile Fabrics and Yarns.

THIS invention consists of a mode or modes of waterproofing and finishing certain textile fabrics and yarns made of wool, silk, hair, and such like animal substances, or a mixture of all or any of those substances, with cotton, flax, or such like vegetable matters, or any of those materials, with other fibrous materials, by rendering them to a certain extent repellent of water, and imparting to them a finish of a lustrous or metallic appearance. To effect this purpose, the fibres of the fabrics or yarns are impregnated with a salt or a compound of a metal, one of the following being preferred,—acetate, nitrate or chloride of copper; acetate and nitrate of lead; nitrate and acetate of bismuth; or any other salts or compounds of those metals except the sulphates. The fabrics or yarns so impregnated are then subjected to the action of steam, charged or mixed with sulphuretted hydrogen gas, or other volatile compound of sulphur. In order to impregnate the plain, dyed, or printed fabrics or yarns with one of the above-named acetates, nitrates and chlorides, or other salt or compound of the metals aforesaid, the goods are immersed in a bath containing a solution of any of the above-named acetates, nitrates and chlorides, or any other salts or compounds of the above metals, of a specific gravity of from one-eighth of a degree to three degrees of Twaddle's hydrometer. If the solution be heated, the fabric or yarn will be more speedily impregnated; but some description of printed or dyed goods will not bear the application of heat without injuring the colours; and in such cases therefore the solution must be used cold, or at a temperature sufficiently low to avoid injury to the colour or colours, the time of immersion being proportionately lengthened. When the solution is heated to a high

temperature (say about 200° F.), and the goods are not very thick, a sufficient impregnation will generally be effected in a few minutes; but if the solution be cold, or the goods very thick, it may be necessary to continue the immersion from two to three hours to ensure a perfect impregnation. Instead of simply immersing the fabrics or yarns in the solution, mechanical action or agitation may also be applied, for the purpose of expediting or ensuring a uniform impregnation of the whole of the goods immersed. After impregnation, the fabrics or yarns are rolled or pressed, in order to deprive them as much as possible of the superfluous solution which they contain, and prevent waste. The fabrics or yarns are then washed; and afterwards the water is expressed from them by rollers, a press, or a hydro-extractor. If the goods be thin or fine, or of a delicate colour, they should be partially dried before being subjected to the action of sulphuretted hydrogen, or any other volatile compound of sulphur, for the purpose of promoting a more uniform action of those agents.

If it be desired to impart a water-repellent property or finish of a lustrous appearance to some parts only of the plain or previously-dyed fabrics or yarns, that object may be effected in two modes; by which also a pattern or ornamental appearance, or variety of effect, may be produced. According to one of these modes, the plain or previously-dyed fabrics or yarns are first impregnated with any of the acetates, nitrates, and chlorides of copper, lead, and bismuth above named, or any other salts or compounds of those metals except the sulphates, and washed, pressed, and dried in the manner above described, by means of printing-blocks or rollers, or any other convenient means. Those parts of the fabrics or yarns which are not to be rendered water-repellent or to have a lustrous appearance, are covered, by printing-blocks or otherwise, with some material which will protect them from the action of sulphuretted hydrogen, or any other volatile compound of sulphur, during the operation hereinafter described. This protecting material may be British gum, or any other material sufficient to afford the requisite protection, and made up into a paste of about the same consistence as the printing-colours used in printing textile fabrics; the fabrics or yarns being then dried, will be ready to be subjected to the action of the steam and sulphuretted hydrogen, or any other volatile compound of sulphur, as hereinafter described. The other of these two modes consists in applying an acetate, nitrate or chloride, or any other salt or compound of the above-named metals, to those parts of the surfaces of the plain or previously-dyed fabrics or yarns which are intended to be made water-repellent, or have a finish of a lustrous appearance. This is done by mixing up the salt or compound of the metal intended to be used with a small quantity of British gum, or any thickening substance, to about the same consistence as the printing-colours above-mentioned; and then, by means of printing-blocks, printing-rollers, or other convenient means, impressing a portion of the mixture of salt or compound and gum or thickening upon the parts to which the lustrous finish is to be imparted. The fabrics or

yarns being then dried are ready to be submitted to the action of the steam and sulphuretted hydrogen, or any other volatile compound of sulphur. Plain fabrics and yarns, intended to be dyed or printed with any colour or colours, may be dyed with, or the colours may contain or be composed in part of any of the acetates, nitrates, or chlorides of copper, lead or bismuth, or any other salts or compounds of those metals except the sulphates. The plain fabrics or yarns which have been dyed with the acetate, nitrate, chloride, or other salts or compounds of copper, lead, or bismuth except the sulphates, are then to be subjected to the action of sulphuretted hydrogen, or any other volatile compound of sulphur and steam, for the purpose of decomposing or acting chemically upon the metallic acetate, nitrate, chloride, or other salt or compound with which they may have been dyed, or enter into the composition of the colouring matter fixed thereon, and so imparting a water-repelling property, or bright, lustrous, or glossy finish to the colours or fibres of the fabrics or yarns. The process of producing a metallic sulphuret on or in the yarn or fabric, may be effected by enclosing the yarn or fabric in a steam-chest or chamber, and then introducing steam impregnated or mixed with sulphuretted hydrogen, or any other volatile compound of sulphur; or the sulphuretted hydrogen and steam may be introduced without first mixing them. The steam or mixture of sulphuretted hydrogen, or any other volatile compounds of sulphur and steam, should be injected into the chest or chamber until the requisite chemical action has been produced, which will generally be effected in from five to thirty minutes. Sulphuretted hydrogen, or any other volatile compounds of sulphur, may be applied. The fabrics are rolled together in a wrapper round steam-cylinders, such as are usually employed in print-works for steaming goods, the sulphuretted hydrogen gas being introduced into the centre of the cylinder together with the steam; or the steam itself may be impregnated with sulphuretted hydrogen, or any volatile compound of sulphur, previous to its introduction into the cylinder: or round the cylinder, together with the wrapper, is rolled a piece of flannel or calico, moistened with a solution of an alkaline sulphuret, or any other sulphuret or compound that will yield volatile compounds of sulphur or sulphuretted hydrogen; but it is preferred to use one of the sulphurets of potassium, sodium, ammonium, calcium, magnesium, barium or strontium, and on such saturated cloth to place another wrapper of flannel or calico, and then the fabric to be operated upon; all these being rolled round the cylinder at the same time. The whole is then covered with a thick wrapper of the above materials, and submitted to the action of steam, during a space of time varying from five to thirty minutes. The fabrics or yarns may then be washed, dried, and treated after the ordinary methods, so as to prepare them for the market, according to the purpose to which they may be intended to be applied.—

Sealed March 8, 1854.

THE CHEMICAL GAZETTE.

No. CCXCV.—February 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Tellurmethyle. By F. WÖHLER and J. DEAN.

THE tellurmethyle was prepared by a process exactly analogous to that for the preparation of telluræthyle*, by the distillation of telluride of potassium with a tolerably concentrated solution of sulphomethylate of baryta. The formation took place very easily, and the distillation was continued as long as oily drops passed over with the water.

Tellurmethyle is a pale yellow mobile liquid, heavier than water, with which it does not mix. It possesses an extremely unpleasant alliaceous odour, which is so intense as to affect the breath of those engaged in working on it for some time. The boiling-point is 82° C.† The gas is yellow, like that of tellurium. It fumes in contact with the air, in consequence of a slight oxidation. It burns with a clear, shining, bluish-white flame, forming at the same time thick clouds of tellurous acid.

Like telluræthyle, it comports itself as a radical—as a metal. It forms a basic oxide, and the corresponding haloid compounds. Direct analysis of it was considered superfluous, since its composition could be more certainly ascertained from its compounds, which are easier to analyse.

Oxide of Tellurmethyle is formed when tellurmethyle is warmed with moderately strong nitric acid. It crystallizes in large colourless prisms; easily soluble in water and in alcohol. When heated, it is decomposed with detonation. Although all the compounds were prepared from the oxide, it is best obtained by the decomposition of the chloride or iodide of the base with oxide of silver. When dry, it is indistinctly crystalline. It deliquesces when exposed to the air, absorbing at the same time carbonic acid. It has a horrible taste, but is without smell. Its solution is strongly alkaline to test-paper. It is so strong an alkali, that at ordinary temperatures it expels ammonia from sal-ammoniac, and produces a blue precipitate with sulphate of copper. Out of its solution sulphuric acid educes

* Chem. Gaz., vol. xi. p. 49.

† Probably the boiling-point is at 80° C., for during the experiment the thermometer did not dip into the liquid, but into the oil in which the thin tube containing the tellurmethyle was placed. If 80° C. be taken as the boiling-point of tellurmethyle, according to Kopp's law the boiling-point of telluræthyle must be at 99° . This has not yet been determined by experiment.

tellurmethyle; hydrochloric acid, a white chloride of tellurmethyle; and hydriodic acid, red iodide.

Sulphate of Oxide of Tellurmethyle crystallizes in clear, tolerably large, regular cubes; soluble in water, insoluble in alcohol.

The salts of oxalic, tartaric, acetic, and formic acids are all readily soluble.

Chloride of Tellurmethyle is formed as a dense white precipitate when hydrochloric acid is added to a solution of the nitrate of the base. On warming, it is dissolved, and on again cooling, crystallizes out in long thin prisms, like those of bichloride of mercury. It melts at $97^{\circ} \cdot 5$ C.; solidifies crystalline; is easily soluble in alcohol; forms no precipitate with bichloride of platinum.

Oxychloride of Tellurmethyle, $C^2 H^3 Te, Cl + C^2 H^3 TeO$, is formed by dissolving the chloride in ammonia. It forms short colourless prisms. Hydrochloric acid precipitates from its solution the chloride.

Bromide of Tellurmethyle, $C^2 H^3 TeBr$, is formed like the chloride, with which it is entirely analogous.

Iodide of Tellurmethyle, $C^2 H^3 Te, I$.—When hydriodic acid or iodide of potassium is added to a solution of the nitrate of the base, a bright saffron-yellow precipitate results, which becomes after some moments vermilion-red. When the solutions are mixed together warm, the precipitate is formed directly red and crystalline. When dried, it forms a vermilion-red powder.

The iodide was used for determining the composition of the base. The carbon and hydrogen were determined by combustion with oxide of copper; the iodine by precipitation with nitrate of silver; the tellurium by decomposing the compound with aqua regia, evaporation to dryness, and precipitation of the tellurium with sulphite of ammonia:—

	Found.	Calculated, $C^2 H^3 TeI$.
Carbon	5·40	5·81
Hydrogen	1·61	1·45
Tellurium	31·24	31·12
Iodine	61·54	61·62

In cold water the iodide is only slightly soluble, much more so in warm. It is dissolved in hot alcohol in great quantity, with orange-yellow colour, and crystallizes out on cooling in small, shining, vermilion prisms. Under the microscope they appear transparent, with orange-yellow colour, and certain faces show a beautiful blue surface colour*. When the cold alcoholic solution is mixed with an equal volume of water, the iodide falls as a citron-yellow precipitate; after a few minutes a movement of the particles takes place, and shortly the whole precipitate is changed into small glittering scales of vermilion colour. Manifestly this body, like iodide of mercury, has two conditions, a yellow and a red, and probably, like that salt, is also dimorphous. The authors were unsuccessful in obtain-

* Prof. Haidinger has undertaken to determine their optical relation and form more minutely.

ing the yellow modification in a fixed and crystalline form. By spontaneous evaporation of the alcoholic solution, in which it is evidently contained in the yellow form, red crystals are obtained, and without decomposition it does not melt. Even at 130°C . it is converted into black iodide of tellurium.

There appears to be a sulphide of tellurmethyle, which from want of material the authors were unable to study more minutely. When sulphuretted hydrogen is passed into solution of chloride of tellurmethyle, a white flocky precipitate is produced ($\text{C}^2\text{H}^3\text{TeI} + \text{C}^2\text{H}^3\text{TeCl?}$), which becomes afterwards yellow, while the liquid assumes an extremely loathsome smell. If the liquid is now distilled, a heavy oily body of reddish-yellow colour passes over along with the water. This body possesses an extremely disagreeable odour. When oxidized with aqua regia, it gives sulphuric acid. When solution of oxide of tellurmethyle is saturated with sulphuretted hydrogen, a feeble white cloudiness results. If the liquid be now distilled, as soon as the heat begins to act, white sulphur separates, and a yellow oil passes over, which appears to be merely reduced tellurmethyle.—*Nachrichten von der Koniglichen Gesellschaft der Wissenschaften zu Göttingen*, No. 1, 1855.

On the Fat of Myristica Otoba. By E. URICOECHEA.

The author has investigated the fat obtained by pressing the fruit of the *Myristica Otoba*. The fruits have the same taste as the nutmeg. It is employed in New Granada, principally as an application in skin diseases of horses.

The fat, which is called *Otoba* in New Granada, is not quite colourless; it is butyraceous, and when fresh smells like nutmeg. When fusing, it evolves a peculiar unpleasant odour. The fat melts at 100°F ., whilst the fat of the common nutmeg melts at 124°F . Alcohol extracts from it a fat identical with that of the common nutmeg, with a melting-point of 115°F . On saponification it furnished glycerine. The soap was dissolved in alcohol, and partially precipitated, according to Heintz's method, with acetate of magnesia; the separate precipitates were then decomposed by muriatic acid, the fatty acids washed with water, and purified by recrystallization from alcohol. The acid of the first precipitate melted at $94^{\circ}\cdot 5\text{F}$., that of the second and third at $95^{\circ}\cdot 4\text{F}$. They were consequently identical with myristic acid, the melting-point of which, according to Heintz, is $96^{\circ}\cdot 8\text{F}$. (94°F Playfair). The analysis also agreed with the formula $\text{C}^{28}\text{H}^{20}\text{O}^4$.

When the precipitate of myristate of magnesia has been decomposed and the myristic acid dissolved by alcohol, a residue is left. This is a new body, to which the author gives the name of *Otobite*. After it was purified by recrystallization from hot alcohol and æther, its composition was $\text{C}^{24}\text{H}^{18}\text{O}^5$. It is inodorous and tasteless. insoluble in water, and crystallizes in good-sized shining prisms. It fuses at $271^{\circ}\cdot 4\text{F}$., and solidifies again in a crystalline form. When heated beyond this point, it solidifies in an amorphous form. Heated

on platinum foil, it evolves aromatic fumes, and then burns with a smoky flame. Its analysis gave,—

Carbon	73·19	72·86	24	73·09
Hydrogen	6·35	6·46	13	6·59
Oxygen	20·46	20·68	5	20·30

Liebig's *Annalen*, xci. p. 369.

On the Compounds of Grape-sugar with Chloride of Sodium.
By G. STÆDELER.

Peligot, to whom we are indebted for a series of very careful investigations of the different kinds of sugar, states that the quantity of sugar in diabetic urine may rise to 10 per cent.; one patient furnished more than 2 kilogrms. of grape-sugar daily. Such an abundant secretion as this probably only occurs in rare instances; the highest amount hitherto observed by the author was a little more than 8 per cent.

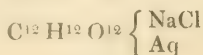
This urine contained only a very small proportion of other substances, except sugar, chloride of sodium and a little urea; and the author therefore employed it in the preparation of the compound with chloride of sodium, which, according to Pasteur's observations, does not belong to the hexagonal system, as was formerly supposed, but to the rhombic system.

By the gradual evaporation of the urine after saturation with chloride of sodium, the author obtained crystals which were not exactly similar in different crystallizations; they were for the most part well formed, but the surfaces were not sufficiently polished to enable them to be measured exactly. The determination of the amount of chloride of sodium soon showed, that besides the well-known compound, one, or perhaps even two others exist; and this is probably the reason that Pasteur's measurements do not agree with those of previous authors.

By far the greater portion of the crystals obtained contained on the average 23 per cent. of chloride of sodium, agreeing nearly with the proportion 1 equiv. chloride of sodium to 1 equiv. of grape-sugar. The analysis gave the following results, represented by the formula $\text{NaCl}, \text{C}^{12} \text{H}^{12} \text{O}^{12}$:—

	I.	II.			
Chloride of sodium	23·01	23·01	1 =	58·5	23·64
Carbon	28·71	28·91	12	72·0	29·09
Hydrogen	5·28	5·3	213	13·0	5·25
Oxygen	43·00	42·76	13	104·0	42·02

When heated to 266° – 284° F., the compound lost 1 equiv. water = 3·64 per cent.; found, 3·55 per cent. It may be regarded as crystallized grape-sugar, in which 1 equiv. of water of crystallization is displaced by chloride of sodium :—

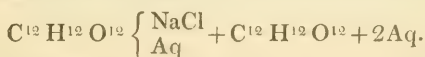


Calloud, who first observed that the grape-sugar of honey combined with chloride of sodium, found that the amount of the latter varied between 8·3 and 25 per cent. No value has been attached to these determinations, but certainly without reason, for the crystals with the highest amount of chloride of sodium were undoubtedly the compound above described.

The author also obtained crystals, the amount of chloride of sodium in which stood between that of compounds with 1 and 2 equivs. of sugar; it appears consequently that both compounds may crystallize together. He also found crystals, the amount of chloride of sodium in which rose considerably above 23·64 per cent.; the proportions approached the formula $C^{12}H^{12}O^{12} + 2NaCl$. These crystals were very small, and always contained some water (1·1–1·5 per cent.). It is possible however that these were nothing but the compound $C^{12}H^{12}O^{12} \left\{ \begin{smallmatrix} NaCl \\ Aq \end{smallmatrix} \right.$ with enclosed crystals of chloride of sodium, although the eye could not distinguish any heterogeneous constituents.

Erdmann and Lehmann have calculated that the compound of chloride of sodium with 2 equivs. of grape-sugar has the formula $2(C^{12}H^{12}O^{12}) + NaCl + 2Aq$, as it loses 2 equivs. of water *in vacuo* or at 212° F. Peligot found however that a third equivalent of water was expelled at 320° F., and this was confirmed by Erdmann.

There can consequently be no doubt, that instead of 2, the compound contains 3 equivs. of water; it is only a combination of the compound analysed by the author with hydrated grape-sugar:—



By the combustion of 1·192 grm. of the compound, dried at 212° F., Erdmann obtained 1·491 grm. of carbonic acid and 0·627 grm. of water = 34·11 per cent. carbon and 5·85 hydrogen. The formula $C^{12}H^{12}O^{12} \left\{ \begin{smallmatrix} NaCl \\ Aq \end{smallmatrix} \right. + C^{12}H^{12}O^{12}$ requires 33·68 per cent. carbon and 5·85 per cent. hydrogen. To explain the difference of 0·43 per cent. in the amount of carbon, we need only recollect that Calloud found 8·3 per cent., and the author 11·64 and 12·41 per cent. of chloride of sodium in well-formed crystals. Such crystals, of course, give an excess of carbon in analysis, whilst the hydrogen is not perceptibly increased.—*Mittheil. der Naturf. Gesellsch. in Zürich*, 1854, p. 468.

On Thuja occidentalis. By A. KAWALIER.

The green parts of the *Thuja* were extracted by boiling with alcohol of spec. grav. 0·828; the alcoholic decoction, which had a strong green colour, became turbid on cooling. Voluminous yellow flakes of a waxy matter separated; these were collected on a filter. The filtrate was distilled on the water-bath, and after the greater part of the alcohol had been distilled off, water was added to the

residue, and the distillation was continued until all the alcohol had passed over.

The distilled alcoholic liquid is of a yellowish colour, and has a peculiar odour, both arising from the essential oil of the *Thuja*. The residue in the retort consists of a turbid watery fluid, and a green, sticky, resinous mass, which sinks to the bottom.

The watery liquid is coloured green by salts of peroxide of iron; with solution of acetate of lead it gives a yellow precipitate, which contains a yellow, crystallizable, tannic acid. The fluid filtered from the lead precipitate furnished a dingy yellow precipitate when treated with basic acetate of lead whilst boiling hot; this contains an amorphous tannic acid, with traces of an acid which appears to be citric acid.

The liquid filtered from this second lead salt was decomposed by sulphuretted hydrogen, and the clear solution salt filtered from the sulphuret of lead. It contains sugar and a bitter matter.

If the green parts of the *Thuja*, which have been extracted by alcohol, are afterwards boiled with water to which a trace of alkali has been added, a decoction is obtained, from which a gelatinous mass is thrown down on the addition of an acid.

Of the substances just mentioned, several are identical with those found by the author in *Pinus sylvestris*.

Pinipicrine.—The author gives this name to a bitter matter which is contained both in the *Thuja* and in *Pinus sylvestris*. Its mode of preparation was described by the author in his investigation of the latter plant. It is decomposed by acids into sugar and ericic-nole. The analysis of the pinipicrine of *Thuja* gave—

Carbon	55.45	44 =	264	55.46
Hydrogen	7.62	36	36	7.56
Oxygen	36.93	22	176	36.98

Sugar.—The sugar remains undissolved in the mixture of anhydrous alcohol and æther used in the preparation of pinipicrine.

Gelatinous Matter.—The gelatinous matter was prepared in the same way as that of the leaves of *Pinus sylvestris*. Its analysis gave—

Carbon	43.33	43.28	16 =	96	43.64
Hydrogen	5.45	5.52	12	12	5.45
Oxygen	51.22	51.20	14	112	50.91

This jelly therefore possesses the same composition as that obtained from the bark of *Pinus sylvestris*, whilst the composition of the jelly from the epidermis of the leaves of *Pinus sylvestris* is expressed by the formula $C^{16}H^{10}O^{10}$.

Wax.—The bark of *Pinus sylvestris* contains a wax which has the composition of palmitic or æthalic acid, but differs greatly in its properties from those acids. The wax of the leaves of *Thuja* has the same composition.

The yellow flakes which separated on the cooling of the alcoholic

decoction of *Thuja*, were filtered and purified by repeated solution in boiling alcohol, with admixture of animal charcoal. The analysis of the pure white wax gave the following numbers:—

Carbon	74.96	32 =	192	75.00
Hydrogen	12.30	32	32	12.50
Oxygen	12.74	4	32	12.50

As this wax was still yellowish when melted, a portion of it was dissolved in hot alcohol of spec. grav. 0.828, and mixed with an alcoholic solution of acetate of lead, both for further purification and to separate it into an acid and neutral portion. Only a trace of a precipitate was produced; this was separated by filtration. The hot filtered solution deposits pure white flakes on cooling. These were collected on a filter, suspended in alcohol, and decomposed by sulphuretted hydrogen; the fluid was then heated to boiling with the sulphuret of lead, and filtered whilst boiling. The filtrate, when evaporated on the water-bath, left the wax perfectly colourless. Its composition, on analysis, was the same as before this operation.

The portion of wax deposited on the cooling of the decoction of *Thuja* is, of course, that which is most difficult of solution. The more readily soluble portion remains dissolved in the cold decoction. When the alcohol is distilled from the decoction and the residue is mixed with water, a sticky, green, resinous mass sinks to the bottom, as has already been mentioned. A portion of wax is mixed with this resin. It may be obtained pure in the following manner. The resinous mass is dissolved in boiling alcohol of spec. grav. 0.828; an alcoholic solution of acetate of lead is then added, when a sticky precipitate, which is at first yellow, but afterwards becomes green, is produced. This precipitate is washed with alcohol, and decomposed under alcohol by sulphuretted hydrogen; the fluid is heated with the sulphuret of lead, filtered through a funnel surrounded with hot water, and the filtrate allowed to cool. Yellow flakes of wax separate, which are purified by repeated solution in hot alcohol with addition of animal charcoal. As the wax was always changed by oxidation when dried at 212° F., it was dried *in vacuo*. Analysis:—

Carbon	74.87	32 =	192	75.00
Hydrogen	12.59	32	32	12.50
Oxygen	12.54	4	32	12.50

It had consequently the same composition as the portion first separated. Hence it follows that the wax of *Thuja*-leaves has the same composition as that of the bark of *Pinus sylvestris*.

The wax, mixed with soda lime in a retort, and heated on the oil-bath to 464°–482° F., gave a little water and traces of a fatty oil which had a soap-like odour. The contents of the retort, cooled without access of air, were triturated and extracted with a large quantity of cold water. The watery solution, separated from the insoluble part by filtration, furnished a white flocculent precipitate on the addition of muriatic acid; this, when washed with water, melted, and dried at 212° F., had the following composition:—

Carbon	68.10	36 =	216	68.35
Hydrogen	11.19	36	36	11.39
Oxygen	20.71	8	64	20.26

The portion of the contents of the retort which was insoluble in water, was dried on the water-bath, finely pounded, and extracted with æther. The residue, after exhaustion with æther, was decomposed by water containing muriatic acid. The acid of the lime salt soon separates, and floats on the solution of chloride of calcium. It was dissolved in water containing ammonia, treated with animal charcoal, and precipitated from the solution by muriatic acid. Analysis:—

Carbon	72.41	36 =	216	72.48
Hydrogen	11.88	34	34	11.41
Oxygen	15.71	6	48	16.11

This is the composition of the oleic acid of the fluid oils, from which this solid body differs widely in its properties.

The wax from the leaves of *Pinus sylvestris*, to which the author has given the name of *ceropinic acid*, agrees in its composition with the formula $C^{36}H^{34}O^5$, and is only distinguished from the present waxy acid by its smaller quantity of oxygen. The acid which was obtained from the watery solution of the contents of the retort contains the elements of 2 equivs. of water more than the acid of the lime salt,—



The ætherial extract of the lime salt (before its decomposition) leaves, after the volatilization of the æther, a white, waxy, cracked, brittle mass, the analysis of which gave—

Carbon	79.85	36 =	216	80.00
Hydrogen	14.01	38	38	14.07
Oxygen	6.14	2	16	5.93

The formula $C^{36}H^{38}O^2$ expresses the constitution of the alcohol of stearophanic acid, so that the acid of the lime salt, $C^{36}H^{34}O^6$, may be considered as stearophanic acid in which 2 equivs. of hydrogen have been displaced by oxygen; thus $C^{36}H^{36}O^4$ stearophanic acid— $2H + 2O = C^{36}H^{34}O^6$, the acid of the lime salt.

According to this mode of decomposition, the acid of the wax must not be expressed by the formula $C^{32}H^{32}O^4$, but would agree with the formula $C^{216}H^{211}O^{27}$.

The wax of the *Thuja* was boiled for a considerable time with solution of potash; the mass, which could not be filtered, was mixed with solution of chlorides of sodium and calcium, and washed with water on a filter. The addition of muriatic acid to the fluid which passed threw down flakes, which could be decomposed into several products by treatment with alcohol; the purity of these is however very doubtful. The portion insoluble in water was dried and exhausted with æther. On the evaporation of the latter, a residue was obtained, which was separated by treatment with boiling alcohol into two portions, one difficult of solution, the other rather more soluble:—

Carbon.....	79·27	79·53	58 = 348	79·45
Hydrogen	13·22	13·13	58 58	13·24
Oxygen	7·51	7·34	4 32	7·21

This substance therefore has the composition of ceropinic æther, without however being identical therewith.

The lime soap, which had been exhausted with æther, was decomposed with water containing muriatic acid. The waxy acid separated was dissolved in a mixture of alcohol and æther, and treated with animal charcoal to get rid of its yellowish colour. When the æther was expelled from the solution, some flakes separated; these were removed by filtration. When the alcohol was slowly evaporated, the acid was deposited in cauliflower-like groups of small crystals. Analysis:—

Carbon.....	70·01	70·37	58 = 348	70·44
Hydrogen	12·02	12·02	58 58	11·74
Oxygen	17·97	17·61	11 88	17·82

When a portion of this acid is dissolved in water containing ammonia, and the solution is precipitated by solution of chloride of barium, a baryta salt of this acid is obtained in the form of white, somewhat slimy flakes; these were dried *in vacuo*, and gave on analysis—

Carbon	54·20	58 = 348·000	54·54
Hydrogen	9·04	57 57·000	8·93
Oxygen	12·45	10 80·000	12·54
Baryta	24·31	2 153·066	23·99

Another portion of the wax was treated with soda lime, the mass extracted with water, the insoluble residue dried and exhausted with æther; the lime salt was decomposed by muriatic acid and analysed:—

Carbon.....	70·06	58 = 348	70·31
Hydrogen.....	11·95	58 58	11·91
Oxygen.....	17·99	11 88	17·78

A solution of the acid in hot alcohol of spec. grav. 0·828, was mixed with water until a considerable turbidity was produced; ammonia was then added until the turbidity disappeared, and the clear fluid was precipitated with chloride of barium. The gelatinous precipitate was dried *in vacuo*. Analysis gave—

Carbon	53·69	58 = 348·000	53·78
Hydrogen	9·02	58 58·000	8·96
Oxygen	13·80	11 88·000	13·61
Baryta	23·49	2 153·066	23·65

After deducting the baryta, there remains for the acid 70·17 per cent. C, 11·79 per cent. H, and 18·04 per cent. O.

The waxy body extracted from the lime salt of this acid by æther, purified by repeated recrystallization from alcohol, gave on analysis—

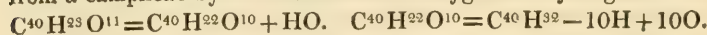
Carbon	80.75	42 =	252	80.77
Hydrogen	14.01	44	44	14.10
Oxygen	5.24	2	16	5.13

Judging from this decomposition, the wax of the *Thuja* must consist of a compound of $C^{42}H^{41}O$ and $C^{58}H^{57}O^{11}$.

Resins.—The alcoholic decoction of *Thuja*, after the distillation of the alcohol and the addition of water, deposits a green sticky resin mixed with a little wax; this, when dissolved in alcohol of spec. grav. 0.828, and mixed with an alcoholic solution of acetate of lead, furnishes a precipitate in which the portion of wax is contained. The green fluid filtered from the lead precipitate is treated with sulphuretted hydrogen to remove the lead. The sulphuret of lead takes up all the chlorophylle, so that the filtrate appears yellow. If the alcohol be distilled from this fluid, a semifluid resin separates, which is dissolved in very dilute solution of potash. The clear brown solution is completely precipitated with solution of chloride of calcium; the yellow precipitate is separated from the solution by decantation, agitated with a large quantity of water, and collected on a filter. The mother-liquor and the whole of the washing-water are put together and mixed with muriatic acid, which produces a precipitate in the form of voluminous, yellowish-white flakes. These are collected on a filter, washed with water, and again dissolved in lime water. The brownish-yellow colour cannot be got rid of by animal charcoal, but the substance may be purified in the following manner:—A stream of carbonic acid gas is passed into the solution as long as a precipitate is produced; the fluid is then filtered from the precipitate and precipitated by muriatic acid. As long as this precipitate remains flocculent it is white, but when it cakes together it becomes yellow. This mass dissolves entirely in æther, and remains, after the evaporation of the latter, in the form of a transparent resinous mass, which may be reduced to a citron-yellow powder by trituration. Its analysis gave—

Carbon	68.39	40 =	240	68.37
Hydrogen	6.78	23	23	6.55
Oxygen	24.83	11	88	25.08

This body may be regarded as the hydrate of a compound formed from a camphene by the substitution of oxygen for hydrogen—



The precipitate produced in the above-mentioned fluid by carbonic acid is washed with water, dried on the water-bath, and extracted with æther; the residue is carbonate of lime. The ætherial solution, evaporated on the water-bath, leaves a pale yellowish, brittle mass, which when triturated forms a white, very electrical powder; its analysis gave—

Carbon	70.82	24 =	144	70.93
Hydrogen	9.33—9.46	19	19	9.36
Oxygen	19.85	5	40	19.71

The properties and composition of this body show that it is iden-

tical with the substance found in the leaves of *Pinus sylvestris*, to which the author gave the name of *chinovous acid*.

The precipitate produced by chloride of calcium in the alcoholic solution of the resin dissolves for the most part in æther after drying. The residue left after the evaporation of the æther dissolves partially in alcohol of spec. grav. 0.828. The insoluble portion contains a little of a blackish-brown resin and a large quantity of lime. The dissolved portion was purified by distilling off the alcohol, and treating the residue with water containing muriatic acid. There remains a semifluid, sticky resin, of a brownish-yellow colour, and containing a very small amount of oxygen; this however still appeared to be a mixture of several bodies, and the author does not give its analysis.

Tannic Acids.—The tannic acids of *Thuja occidentalis* are contained in the watery fluid from which the resin and wax have separated. This fluid gives a precipitate with solution of acetate of lead, which contains the principal portion of the crystallizable tannic acid, whilst the greater part of the amorphous acid is contained in a precipitate formed in the hot mother-liquor on the addition of basic acetate of lead; this is accompanied by a small quantity of an acid, which appears to be citric acid.—*Sitzungsbericht der Akad. der Wiss. zu Wien*, xiii. p. 514.

On the Detection of Prussic Acid in the Human Body three weeks after Death. By M. BRAME.

The author states, that having been called on to examine the body of a young man who had poisoned himself with prussic acid, he succeeded in recognizing the poison, and obtaining a considerable quantity of it, from the contents of the stomach three weeks after death.

On the addition of pure neutral nitrate of silver, a yellowish flocculent precipitate was formed in abundance, which, when well washed, dried *in vacuo*, and afterwards heated for a few moments on the sand-bath, acquired a grayish colour. It was soluble in ammonia and cyanide of potassium. When decomposed by potassium with the aid of heat, it formed cyanide of potassium, from which prussic acid and prussian blue were easily obtained. When suspended in water and submitted to the action of sulphuretted hydrogen, it furnished a limpid solution of prussic acid, after the sulphuret of silver formed had been separated by filtration. By means of muriatic acid, prussic acid of a very strong odour was obtained from it, the vapour of which received in a solution of nitrate of silver produced a white precipitate, which was soluble in ammonia. The original precipitate, heated by the spirit-lamp in a tube closed at one end, furnished prussic acid. The same precipitate, gently heated with caustic potash, gave rise to no evolution of ammonia.

The prussic acid had consequently remained in the stomach three weeks after inhumation. It did not appear to have entered into any chemical combination. Its quantity was pretty considerable, for the author collected 0.60 gr. of cyanide of silver, representing about 0.120 gr. of prussic acid.—*Comptes Rendus*, Nov. 13, 1854, p. 968.

On the Compounds of Chlorine with Iodine. By J. TRAPP.

Besides the simple chloride of iodine, ICl , and the triple chloride, ICl_3 , the preparation and properties of which are well known, the author has obtained and analysed a compound isomeric with the fluid chloride of the formula ICl .

It is produced by heating iodine to fusion in a retort, and then passing a rapid current of chlorine into the vapour of iodine. The retort must be strongly heated during the introduction of the chlorine, and the chlorine must only be passed in until all the iodine in the retort has disappeared. During the operation, the neck and upper part of the retort should be filled with thick reddish-brown fumes.

In this manner the new compound is obtained in large prisms and tables, often an inch in length; the crystals are perfectly transparent and very shining, especially by candle-light; they fuse at 77°F. , forming a red oily fluid. They are very volatile, and give an intense and permanent brown colour to organic materials. Their odour is extremely disagreeable, strong and penetrating, very different from that either of chlorine or iodine. This chloride does not dissolve completely in water; iodine separates in fine needles, and the fluid has an acid reaction. The crystallized chloride dissolves readily in alcohol and æther, with a deep brown colour; the solutions have an acid reaction, and a weaker odour than the solid body. If the alcoholic solution be distilled, a yellow fluid passes over; yellow vapours of iodine are then evolved, which are deposited in acicular crystals in the neck of the retort. The alcoholic solution of this chloride (1 part of chloride of iodine in 3 parts of alcohol of spec. grav. 0.810) distilled with carbonate of potash, furnishes a colourless distillate, of a very unpleasant ætherial odour, and a sweet, but at the same time ætherial taste. Water separates nothing from this distillate; the water itself settles to the bottom.

Analysis proves that this chloride has the composition ICl ; and as the only difference in the preparation of the two chlorides is that the solid chloride is formed at a higher temperature, the author endeavoured, by heating the ordinary chloride of iodine in closed tubes to 248° and 356°F. , to prepare the new chloride; the experiments however gave a negative result; the chloride remained fluid.—*Bull. de St. Pétersb. Classe Phys. Math.*, xiii. p. 13.

On the artificial Production of Cinnamon Oil. By A. STRECKER.

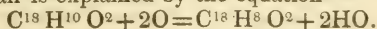
I pointed out some years since, that styrene, which is obtained by treating styracine with a concentrated or alcoholic solution of potash, is the alcohol of cinnamic acid, as it exhibits the same relation with regard to this acid as alcohol to acetic acid. By experiments made at my suggestion, M. Wolff has proved that styrene, under the influence of energetic oxidizing agents, becomes converted into cinnamic acid.

I have found that styrene, in the same conditions in which alcohol

is converted into aldehyde, furnishes the aldehyde of cinnamic acid, or cinnamon oil.

For this purpose it is sufficient to moisten platinum black with liquid styrene, and leave the mixture exposed to the air. In a few days the greater part of the styrene is converted into cinnamic aldehyde, which is separated from the unaltered styrene by the excellent process of M. Bertagnini. With a concentrated solution of bisulphite of potash, crystals are obtained, which are washed with æther to free them from the styrene. The crystals are purified by the addition of sulphuric acid diluted with pure cinnamic aldehyde. The crystals dissolve in nitric acid, and in a few moments crystals are formed of the nitrate of the hydruret of cinnamyle.

The conversion of styroné into hydruret of cinnamyle by the oxygen of the air is explained by the equation—



Styrone.

Hydruret of
cinnamyle.

—*Comptes Rendus*, July 3, 1854, p. 61.

Incineration of Organic Matter.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,—Considerable difficulty is often experienced in perfectly incinerating organic substances, especially if nitrogen be present. The various means employed are all open to objection. The chloride of platinum may occasion a decomposition of carbonates; the nitrate of ammonia, without great care, is apt to scatter a portion of the contents out of the crucible, and nitric acid is exceedingly tedious. I have found the following process very convenient:—A known weight of pure peroxide of barium, dry and in fine powder, is carefully mixed with the substance, and the whole ignited in the usual manner. The resulting baryta does not readily interfere with any subsequent operation.

J. W. SLATER.

Sheffield Mechanics' Institution.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Extraction of Silver, by Augustin's Method, from Copper Matte containing Lead and Zinc. By Prof. PLATTNER.

AUGUSTIN'S method of extracting silver from copper matte, and from the black copper yielded by it, has not under all circumstances proved more satisfactory than eliquation and amalgamation processes. In certain cases the loss of silver has been too great. In the Mansfield Works, where the matte is very pure, Augustin's method was adopted with advantage until superseded by the cheaper method introduced by Ziervogel. The author has investigated the causes of this loss of silver, and particularly how far the sulphides of lead, zinc and antimony, present in an impure matte, consisting

for the most part of sulphide of copper and sulphide of iron, are to be regarded as causes of this loss.

By the roasting of such a matte, these sulphides are at first converted into basic sulphates only; and it is not until afterwards, when the temperature is raised, that they are converted, with the exception of the sulphates already formed, into free oxides, while sulphur acids and oxide of antimony are volatilized; but in the subsequent treatment of the roasted copper matte with chloride of sodium, there are formed, when the matte is impure, besides chloride of silver, several other chlorides, which are partly volatile.

According to general experience, it may be conjectured that these chlorides, in volatilizing, carry away silver. To ascertain whether this is the case, the author has made a series of experiments. The substances to be operated upon were mixed with chloride of sodium, and heated to redness in open glass tubes of sufficient width.

1. *Oxide of Lead* experiences no change by this treatment with chloride of sodium.

2. *Sulphate of Lead* melts, even at a dull red heat, with a quantity of chloride of sodium sufficient for decomposition, to a clear liquid, evolving vapours of chloride of lead, which are more copious the higher the temperature and the greater the current of air.

3. *Oxide of Zinc* experiences no change by this treatment with chloride of sodium.

4. *Sulphate of Zinc* behaves in the same manner as sulphate of lead, forming, even at a dull red heat, a clear liquid, which, when air has access, evolves vapours of chloride of zinc.

5. *Combined Antimonious and Antimonic Acids* (SbO_4), when heated with chloride of sodium to a moderate red heat, yields vapours of chloride of antimony, though not to any considerable amount, even when the current of air is strong.

6. *Sulphate of Copper*, of which there may be a small proportion in a roasted matte, melts, even at a dull red heat, with a quantity of chloride of sodium sufficient for decomposition, to an opaque mass, chloride of copper and sulphate of soda being formed; chloride of copper is vaporized when air has access, although the greater part is decomposed, with evolution of chlorine, even at a faint red heat, into subchloride of copper, which is less volatile than the chloride.

Since chloride of lead and chloride of zinc do not volatilize perfectly at a red heat when air has access, oxychloride of lead being formed from the one, and oxide of zinc from the other, while chlorine is liberated in both cases, and when it comes in contact with water-vapour at a sufficiently high temperature, is converted into hydrochloric acid, the formation of a considerable amount of chloride of copper, together with chloride of lead, in treating with chloride of sodium a perfectly roasted copper matte, almost free from sulphate of copper, is likewise accounted for. When, for example, the vapour of chloride of sodium, diffused throughout the roast-charge, comes in contact with sulphate of lead, a mutual decomposition takes place, there are formed chloride of lead and sulphate of soda, the former of which products is volatilizable. Then

since the roast-charge is constantly stirred, so that fresh portions of the lower layers are brought to the surface, and in contact with the gaseous products of combustion from the fuel, as well as with atmospheric air, a portion of the chloride of lead is vaporized unaltered, while another portion is converted, with evolution of chlorine, into oxychloride of lead, which remains. The chlorine liberated reacts at the moment of its liberation with the water-vapour of the combustion products from the fuel, forming hydrochloric acid, which reacts with the oxide of copper, forming chloride of copper ($\text{CuCl} + \text{Cu}^\circ \text{Cl}$) and water. The chloride of copper is volatilized together with the chloride of lead, a small proportion of it being decomposed at the flue of the roasting-furnace by the water-vapour in the combustion-products of the fuel, so that oxide of copper is deposited there, sometimes in a crystalline state.

The formation of chloride of copper is likewise determined, although perhaps in a somewhat less degree, by chloride of zinc, and in the same manner as by chloride of lead.

Consequently when a copper matte contains sensible quantities of sulphides, which leave some sulphates after roasting, there must be, in the subsequent treatment with chloride of sodium, such a quantity of this substance as will ensure the conversion into chloride of all the sulphate of silver, and any metallic silver or unaltered sulphide of silver that may be present.

Since, moreover, the chlorides volatilized during the treatment with chloride of sodium, and deposited in the condensers, contain a certain proportion of silver, it might be inferred that the volatilization of the chloride of silver is determined by the volatile chlorides formed in the process, and that when the condensers are of too small dimensions, and become too much heated by the gaseous combustion-products of the fuel, admitting too rapid a current of gases and vapour, chloride of silver may even be carried off in this manner into the atmosphere. To ascertain whether or not this is the case, the following experiment was made.

A mixture consisting of—

10.0 grms. oxide of copper,

3.0 grms. chloride of lead, and

0.6 gm. chloride of silver (melted and powdered),

was placed in a porcelain tube, two feet long and three-quarters of an inch inside diameter, so as to form a layer about a quarter of an inch thick in the middle. The tube was placed in a furnace, and one end connected with a gasometer containing atmospheric air and a small vessel containing water, so that, as in the roasting on a large scale, a gentle current of air, sufficiently charged with water-vapour, by passing through the water, might be passed over the mixture. The other end of the tube was connected with a two-necked glass vessel, six inches in diameter, and from this a glass tube, four feet long and three-quarters of an inch in diameter, passed upwards into an inverted glass flask.

When the porcelain tube was heated to dull redness, and a current of moist air passed through it, a brown sublimate was produced

in the cool portion of the glass vessel, which became grayish-white when cold, but the passage of vapour through the glass tube could not be observed. As the heat was continued the sublimate increased, so as to form, after the lapse of an hour, a layer about one-sixteenth of an inch thick near the neck of the vessel connected with the porcelain tube, although the mixture had not been altered in its position, and as the vessel became hot, a sublimate was deposited in the glass tube and in the inverted flask; at last even a small quantity of vapour escaped from the flask into the atmosphere. When the sublimate in the two-necked vessel ceased to increase, the operation was stopped.

The sublimate in the two-necked vessel, and in the end of the porcelain tube, was of a grayish-white colour when cold, and weighed 0·9 grm., or 6·61 per cent. of the mixture operated upon. It was found, by examination with the blowpipe, to consist chiefly of chloride of lead and chloride of copper, with 2·6 per cent. of silver. Analysis in the wet way gave—

per cent.	per cent.
63·8 chloride and oxide of lead.	54·8 lead.
32·8 subchloride of copper.	21·0 copper.
3·4 chloride of silver.	2·6 silver.

The weight of the sublimate in the glass tube and in the flask could not be estimated; it consisted chiefly of chloride of copper, and contained 1·69 per cent. of silver.

It is therefore evident that the chloride of lead formed in the treatment of copper matte with chloride of sodium determines the formation of chloride of copper when copper is present in the state of oxide, and that chloride of silver is volatilized together with the chlorides of lead and copper, passing to some extent into the atmosphere, even when arrangements are made for condensation, and it must be inferred that any considerable amount of lead in a copper matte is prejudicial to the extraction of the silver, whenever the vapours of chlorides passing from the roasting-chamber into the condensers have not a sufficient opportunity for deposition, owing to the presence of hot products of combustion and a rapid current of air.

One of the conditions therefore of the successful application of Augustin's method of extracting silver is, that the matte should be as free as possible from lead, or any of the sulphides, which by the first roasting are converted into sulphates that by the second roasting are either not at all or only imperfectly decomposed into oxides, and form volatile chlorides in the treatment with chloride of sodium. When, from any reason, this condition cannot be obtained in a sufficient degree, the roasting-furnace must be furnished with spacious condensers, in which the vapours of the chlorides will be perfectly deposited.

Although it is difficult to prepare an impure copper matte, containing silver, for the extraction, so far as to admit of its being effected with little waste of silver, there are means of separating for the most part the metals prejudicial to the silver extraction, and at

the same time of concentrating the copper. It is well known that copper has a greater affinity for sulphur than lead, and it is therefore possible, by melting a copper matte, roasted to a certain degree, with appropriate admixtures for converting the iron into slag, to separate the greater part of the lead it contains, with most certainty together with a little copper. The manner in which the bye-product of this concentration, which will always contain silver, is to be worked so as to reconvert the copper into sulphide, and to separate the lead and silver jointly, will depend upon the methods of smelting adopted, and cannot therefore be considered here. When care has been taken to separate zinc from the matte, when the ore contains blende, there is no reason to fear that the concentrated matte will contain any considerable amount of this metal.

It is likewise a question whether it might not be advantageous to remove the obstacle to the condensation of the vapours of chlorides, arising from their mixture with the hot products of combustion, by conducting the treatment with chloride of sodium in furnaces constructed in such a manner that the products of combustion do not enter the working chamber or the condensers. Such furnaces have long been employed with success at Reichenstein (Silesia), for working arsenical pyrites, and are described in Karsten's 'Metallurgy,' vol. iv. p. 585, and Scheerer's 'Metallurgy,' vol. i. p. 110. Still it must be remembered, on the other hand, that in such a furnace the hearth is most strongly heated, and that in the treatment of copper matte with chloride of sodium, it acquires the property of readily disintegrating, in consequence of the decomposition of the sulphates and the chloride of sodium; moreover, when the temperature in the working-chamber is not sufficiently high, and the current of air too feeble, the volatile chlorides formed are only partially removed, and any considerable residue of chloride of lead is in so far disadvantageous, that it dissolves in the solution of chloride of sodium with which the chloride of silver is extracted, and renders the silver precipitated by copper impure; so that, apart from the probably greater consumption of fuel, it would appear to some extent doubtful whether a reverberatory furnace of this kind would answer in the present case. If it is possible to modify the construction of the furnace, so that the temperature of the working-chamber and the current of air may be regulated at pleasure without the hearth being too much heated, it would, apart from the greater consumption of fuel, certainly be preferable to the ordinary roasting-furnace, in which the flame enters into the roasting-chamber.—*Berg- und hüttenm. Zeitung*, 1854, No. 16.

Relative Fuel-value of Alcohol and Wood-spirit.

Bolley has made some comparative experiments to ascertain this point.

The wood-spirit used was slightly yellow and empyreumatic: the density was 0.81; it began to boil at 154° F., and then the boiling-point rose gradually. It had a slight acid reaction, and the colour became darker on the addition of caustic soda or sulphuric acid.

The alcohol had a density of 0·845.

The apparatus employed for these experiments consisted of a lamp for the combustion of the spirit, the burner being surrounded by a cylinder 8 inches in diameter, and a light brass pan supported above the flame for holding the water to be evaporated. Each experiment extended over about two hours. In each, the true quantity of water evaporated and quantity of spirit burnt were observed. The quantity of water, at 212° F., remaining in the pan was likewise observed, the quantity of steam that would have been produced by the heat thus consumed calculated, and added to the quantity of water evaporated. One fraction of the effect—the heat consumed in raising the water from 62° to 212° F.—is not included in the table below:—

		A. Consumption of fuel in grammes.	B. Evaporation of water in grammes.	Ratio of B to A.	Duration of experiment in minutes.
Wood-spirit	{ 1.	98	514°	5·25	101
	{ 2.	133	697	5·25	149
	{ 3.	124	597	4·81	138
	{ 4.	198	782	3·95	165
Alcohol ..	{ 5.	160	680	4·25	104
	{ 6.	178	781	4·38	148
	{ 7.	133	590	4·43	119
	{ 8.	159	687	4·32	170

In the experiments 1, 2, 3 and 6, 7, 8, the distance between the bottom of the pan and the level of the wick was always the same. In order to ascertain the influence of the greater elevation of the pan, it was raised in experiments 4 and 5 about three-quarters of an inch further from the flame. The result showed a loss in this case.

According to the first three and last three data, the heating capabilities of alcohol and wood-spirit are as 43 : 50, or nearly 6 : 7. The prices however were as 8 : 6 ; consequently the cost of evaporating a given quantity of water by means of alcohol would amount to 56, while with wood-spirit it would be only 36 ; or wood-spirit, under such circumstances, would be nine-fourteenths cheaper fuel than alcohol.—*Schweizerisches Gewerbeblatt*, June 1854.

Silicate of Soda as a means of fixing Aluminous and Iron Mordants.
By Prof. BOLLEY.

The use of silicate of soda in calico-printing has the advantage of rendering the colours deeper than when the dung-bath alone is used. In reference to the action of this salt, it is worthy of remark that alkaline silicates exist in cow-dung, which according to Rogers contains 17·5 per cent. of solid substance ; 15 per cent. of this is ash, so that the fresh dung contains 2·6 per cent. of ash, and the ash contains 62·5 per cent. of silica. A large portion of this silica is in the insoluble condition, but the quantity of soluble silica is not inconsiderable. The soluble portion of the ash amounts to 38 per

cent., and of this 12 per cent. is silica, and 10 per cent. potash and soda.

There is therefore reason for regarding silicate of soda as the efficient ingredient of cow-dung. C. Kœchlin found that the constituents of mordants are met with in the dung-bath after being used, and that the alumina is in solution; whence it must be inferred that a part of the aluminous mordant is dissolved in the dung-bath. However, it still remains to be ascertained in what manner this is effected, what the solvent is, and why the alumina is not precipitated by the salts in the dung. But, on the other hand, it is known that aluminous salts, and even alkaline solutions of alumina and phosphate of alumina, are decomposed by silicate of soda, while insoluble silicate of alumina is formed. Considering all these circumstances together, there are grounds for the opinion that the mordant is converted by silicate of soda into an insoluble state, which is wholly unaffected by the dung-bath.—*Schweizerisches Gewerbeblatt*, May 1854.

PATENTS.

Patent granted to Edward Hæffely, for Improvements in the Manufacture of Stannates of Soda, Potash and Ammonia.

To form stannate of soda, the inventor introduces into a metal pan litharge or red lead (other metallic oxides, hereafter named, will produce the same action, but an oxide of lead is preferred), and a solution of caustic soda of commerce, containing about 22 per cent. of alkali, and reduces by the addition of water, or the washings hereafter named, if required; but this dilution is not necessary to the operation, excepting to keep the stannate of soda in solution and above the precipitate. A plumbate or plumbite of the alkali is thus formed, heat being applied for the purpose of hastening the operation. Feathered metallic tin is then suspended in a bag or thrown into the mixture, when immediately the oxygen from the alkaline solution of the oxide of lead passes to the metallic tin, forming stannic acid, which unites with the alkali, whilst metallic lead in a spongy state is precipitated. The proportions used are 16 lbs. of tin, 45 lbs. caustic soda at 70° Twaddle, from 70 to 80 litharge (or 54 red lead). When the tin has entirely disappeared, which will be after several hours' boiling, say from four to five, depending however upon the granulated state of the tin, the fire is withdrawn, and the precipitate allowed to settle. The clear solution of stannate of soda is then decanted, and the precipitate washed with one or two waters (the waters being used for reducing the alkali in future operations, as above stated). The precipitate is thrown on a hot plate of iron or other metal, and the temperature raised to near redness, when it is speedily reoxidized by the atmospheric air, litharge or red lead being thus formed at pleasure, according to the heat and time occupied in the oxidation. The litharge or red lead may again be used for another operation of producing stannate of soda. The patentee also proposes to substitute for the oxide of lead other

metallic or organic oxides possessing the property of transmitting their oxygen, or part of it, to a more oxidizable metal, like hydrate of peroxide of iron, hydrate of peroxide of manganese, manganate of soda, indigo, and others. The precipitates in these cases will be protoxides of the bases, which may be converted, by any known means, into peroxides, to be again used. The advantages of this process are cheapness, rapidity, and regularity of results; and the stannate so formed is of an improved purity, giving superior results to that formed by the known processes, for the purpose of printing or dyeing textile fabrics. Although stannate of soda only has been mentioned in the above description, the same instructions will hold good for the other alkalies, by substituting potash or ammonia.—Sealed March 13, 1854.

Patent granted to W. I. Cookson, for an Improvement in the Reduction of Lead Ores.

This invention has for its object the separation of the sulphur from the ore in such a manner that the desulphurizing agent may be used over and over again; and the sulphur that has been separated from the ore thereby may be economized and used in the production of articles of commerce. This object is effected by operating upon the lead ore in the presence of metallic iron or oxide of iron, which will thus be made to combine with the sulphur, which becomes separated from the lead ore in the process of reduction.

In carrying out this invention, lead ore and metallic iron are first mixed together, and a small quantity of alkali or neutral salt and carbonaceous matter are added thereto. The mixture is then to be subjected to heat in a furnace or in a crucible, or other suitable receptacle. By this means the lead ore will be reduced to a metallic state; and the iron, by uniting with the liberated sulphur, will form sulphuret of iron, which, when exposed to a damp atmosphere, will fall into powder. To this sulphuret of iron in powder sufficient water is added to make it into a thick paste, which may then be worked up and moulded into small pieces by machinery or otherwise. These moulded pieces must be dried at a moderate heat, and then they may be burned as pyrites in an ordinary kiln used for the manufacture of sulphuric acid; or the sulphuret of iron in a powdered state may be burnt or roasted in a suitable furnace for a similar purpose. This burning or roasting operation will reduce the sulphuret of iron to an oxide of iron containing some sulphur, lead and salts. The oxide of iron is then to be crushed and mixed with carbonaceous matter; after which it may be again used as before described in the reduction of a fresh quantity of lead ore, instead of employing fresh metallic iron. By conducting the process with ordinary care and caution, a greater yield of lead may be obtained than by the ordinary reducing process. This result is considered to be due to the presence of lead in the oxide of iron, which has been used for previous operations. Instead of using iron in the metallic state in the first instance, burnt iron pyrites or gossan may be profitably employed as the desulphurizing agent.—Sealed March 8, 1854.

THE CHEMICAL GAZETTE.

No. CCXCVI.—February 15, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Production of Alcohol from Bicarburetted Hydrogen Gas.
By M. BERTHELOT.

I. 1. A LARGE balloon, capable of containing 31 or 32 litres, was filled with pure bicarburetted hydrogen gas; 900 grms. of pure boiled sulphuric acid were then added in several portions, followed by several kilogrammes of mercury, and the whole was then violently shaken for a long time. The gas was gradually absorbed. After 53,000 shocks, the absorption becoming very slow, the operation was stopped; 30 litres of the gas were absorbed. 5 or 6 vols. of water were added to the sulphuric acid, and this was distilled; by repeated distillations and separations by means of carbonate of potash, 52 grms. of alcohol were at last obtained, representing 45 grms. of absolute alcohol. This weight represents three-fourths of the absorbed gas. The remainder was lost in the manipulations.

2. This alcohol presents a somewhat pungent and aromatic spirituous taste and odour, similar to that which is met with in the distillation of the sulphovinates. It distils almost entirely between 174° and 178° F. It burns without residue, with the usual flame of alcohol. It dissolves chloride of calcium in abundance, and mixes with water in all proportions.

3. A quantity of this alcohol corresponding to 3.1 grs. of absolute alcohol, distilled with sulphuric acid and sand, furnished 1.5 litre of gas containing 1.25 litre of pure olefiant gas, that is to say five-sixths of the quantity of olefiant gas represented by this weight of alcohol. These results agree with those furnished by ordinary alcohol.

The olefiant gas thus prepared possesses the normal properties: it is absorbed by ordinary sulphuric acid (3000 shocks), by bromine, and by iodine, forming the characteristic solid iodide. When collected at the proper moment, it furnished by detonation 2 vols. CO_2 , absorbing 3 vols. of oxygen.

4. 10 parts by weight of my alcohol (regarded as absolute alcohol) distilled with a mixture of sulphuric and acetic acids, furnished 20 parts of crude acetic æther. Calculation gives for 10 parts of alcohol, 19 parts of anhydrous acetic æther. This æther, treated with potash at 212° F., was rapidly decomposed, reproducing acetic acid and alcohol, with a perfectly normal odour. The alcohol was reconstituted in this manner for the third time.

Chem. Gaz. 1855.

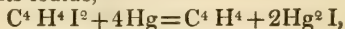
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5. These characters appear to leave no doubt as to the nature of the liquid prepared with olefiant gas. To arrive at greater certainty, the experiments were varied as follows:—

1. The olefiant gas was collected in a gasometer filled with concentrated sulphuric acid. The gasometer, still containing a fourth of the sulphuric acid, was quickly shaken for several minutes; the gas was then passed through mercury into bottles of a litre capacity, and absorbed by boiled sulphuric acid. The complete absorption of the gas required 3000 shocks to each bottle.

2. Olefiant gas, collected and purified in a gasometer filled with sulphuric acid, was passed slowly through fuming sulphuric acid contained in a Liebig's tube. A portion of the gas escaped the action of this fluid, and this portion was absorbed by shaking with ordinary sulphuric acid.

3. Olefiant gas was prepared by the action of mercury and muriatic acid upon its iodide,—



and the gas was absorbed by sulphuric acid.

The sulphuric acid combined with the gas in each of these three operations, was saturated by carbonate of baryta or lime; in this manner sulphovinates were produced.

6. The baryta salt analysed presented the ordinary composition,—



Judging from its properties and crystalline form, this salt is identical with the variety of sulphovinate of baryta which is stable at 212° F.

7. When distilled with acetate of soda, it furnished acetic æther; with butyrate of potash, butyric æther; with benzoate of potash, benzoic æther, $\text{C}^{14} \text{H}^6 \text{O}^4$, $\text{C}^4 \text{H}^4$. The latter boils at 410° F. It was analysed. Treated with potash at 212° F., it reproduced benzoic acid and alcohol. Benzoic æther was also prepared with salts produced by each of the three preceding operations.

8. The fuming acid employed in the second operation furnished a stable and deliquescent calcareous salt (isethionate), which did not yield to benzoic æther. This last observation confirms those of M. Magnus.

9. 100 litres of coal-gas were treated with iodine, and the product obtained heated with a watery solution of potash. In this manner about $\frac{1}{4}$ litre of pure olefiant gas was obtained, which produced by its combustion 2 vols. CO^2 , absorbing 3 vols. of oxygen. This gas was absorbed by sulphuric acid by means of 3000 shocks; it furnished crystallized sulphovinate of baryta, and afterwards benzoic æther; the latter, treated with potash, reproduced benzoic acid and a substance possessing the properties of alcohol.

Bicarburetted hydrogen, therefore, whatever may be its origin, produces æthers and alcohol. This is the first time that alcohol has been obtained without the agency of fermentation.

II. These experiments have been extended to another carburet of hydrogen, propylene, $\text{C}^6 \text{H}^6$, the mode of preparation of which has recently been published by M. Luca and the author*:—

* Chem. Gaz., vol. xii. p. 448.

1. Propylene passed into a Liebig's tube containing boiled sulphuric acid, is absorbed nearly as readily as carbonic acid by potash, but not without evolution of heat. The acid, when diluted with water, filtered and distilled, furnished a spirituous liquid, of a peculiar and penetrating odour, soluble in water, but precipitable from this solution by carbonate of potash.

2. This liquid, when concentrated, but still mixed with water, begins to boil about 178° – 179° F. In this state its density is 0.817; it mixes with water in all proportions; with crystallized chloride of calcium, it forms either an homogeneous solution or two distinct strata, according to the proportion of the salt; the addition of water unites these two strata; but if the mixture be heated, it separates again into two strata, which recombine on cooling.

This liquid burns with a more luminous flame than ordinary alcohol. It presents the properties of propylic alcohol; thus it produces propylene, propylic æthers, and propylosulphate of baryta.

3. Mixed with sulphuric acid and sand and heated, it blackens, becomes decomposed rapidly, and furnishes a considerable quantity of propylene, C^6H^6 , mixed with about one-twentieth of another combustible gas. This gas, which is not absorbable by bromine, appears to be hydruret of propyle, C^6H^8 .

4. If the spirituous liquid be distilled with a mixture of sulphuric and butyric acids, propylobutyric æther, $C^8H^8O^4$, C^6H^6 , is obtained. This compound was analysed; it is a neutral liquid, lighter than water, volatilizable below 266° F., with an odour analogous to that of butyric æther, but more disagreeable; it is completely decomposed by potash at 212° F., reproducing butyric acid and propylic alcohol with their original properties, of odour, action upon water, and chloride of calcium, boiling-point when mixed with water, &c. The weight of this regenerated alcohol nearly equalled three-sevenths of the weight of propylobutyric æther decomposed.

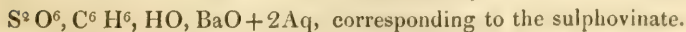
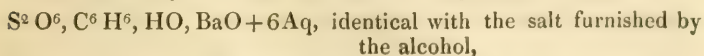
5. The propylic alcohol, distilled with a mixture of sulphuric and acetic acids, furnished propylacetic æther, analogous to acetic æther, but volatile about 194° F.

6. The propylic alcohol, mixed with sulphuric acid, heated slightly, and then saturated with carbonate of baryta, furnished a crystallizable salt, propylosulphate of baryta,—



This salt loses its water of crystallization *in vacuo*. With benzoate of potash it produces propylbenzoic æther.

In other operations, after the absorption of the propylene by the sulphuric acid, the acid, instead of being distilled, was saturated by carbonate of baryta; in this manner the propylosulphate of baryta was obtained crystallized with two different proportions of water:—

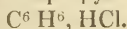


These two hydrates behave in the same manner, both as regards

their stability and their action upon salts. They reproduced propyl-acetic, propylbutyric and propylbenzoic æthers*.

Propylene therefore produces propylic alcohol and its æthers, just as olefiant gas furnishes ordinary alcohol. This formation takes place more readily with propylene.

Considering the particular aptitude for combination exhibited by the latter carburet, the author endeavoured to unite it directly with muriatic acid. Gaseous propylene, left at the ordinary temperature over a stratum of fuming muriatic acid, becomes slowly absorbed, and disappears at the end of a few weeks. This reaction takes place even in a sealed tube. At 212° F. thirty hours were sufficient for its completion. By this means a neutral fluid is formed; it is lighter than water, and insoluble in that menstruum. This fluid, purified by means of potash and distilled, is found to consist principally of a chlorinated body, which is volatile at about 104° F., and possesses the odour, the taste, and the flame of muriatic æther. Its composition agrees with the formula of propylmuriatic æther,—



This experiment is the inverse of M. Thénard's decomposition of muriatic æther. It shows that propylene, like ammonia, is capable of combining directly with muriatic acid and neutralizing it.—*Comptes Rendus*, Jan. 15, 1855, p. 102.

On a peculiar Behaviour of Albuminous Fluids on the addition of Salts. By R. VIRCHOW.

In connexion with the production of dropsy, certain peculiarities of the blood and of the effused fluids have already been frequently the objects of investigation. Amongst the various observations which have served more or less for the explanation of these phenomena, the author lays particular stress upon one made by Robin and Moyse upon the albumen of dropsy.

Thus as Bernard had found that the pancreatic juice possessed the peculiar property of coagulating like solution of albumen by heat, strong acids, alcohol and metallic salts, whilst in other respects it resembles caseine, being coagulable by sulphate of magnesia, Robin and Moyse said that the fluid of ascites and hydrothorax was closely allied to the pancreatic juice, but was distinguished essentially therefrom by the circumstance that the dropsical fluid remained unchanged by the action of chlorine-water, whilst the pancreatic juice acquired a very characteristic red colour with that reagent.

To study this peculiar behaviour of the albuminous fluids, they must be mixed in the cold with a more than their own volume of a solution of sulphate of magnesia and filtered. 3 vols. of water may also be previously added to 1 vol. of the original fluid. In all cases a clear filtrate is obtained; but when serum of the blood or white of egg

* The compound formed by propylene and fuming sulphuric acid did not produce æthers.

is employed, the filtrate coagulates by heat or by the addition of acids, whilst the pancreatic juice does not do this, and the dropsical fluids are only rendered slightly turbid, or at least much less so than previously, by heat, acids and alcohol. If much alcohol be employed, the magnesia salt is precipitated at the same time. From this Robin and Verdeil conclude, that there is a substance which has hitherto been confounded with the albumen of serum; and although its properties are rather anatomical than strictly chemical, they must however be regarded as peculiar.

The author endeavoured to ascertain whether this difference between the albumen of the serum and that of the effused fluids is to be explained by the external circumstances under which the albumen was produced, or whether it depends upon the different composition of the materials in question.

The author ascertained the correctness of the above statements for all the albuminous effusions which he investigated. He confirmed them in the fluids of ascites, hydrothorax, hydropericardium, hydrocele, hydrocephalus, and in albuminous urine; also in the fluid of incipient goitre, but not in the colloid substance of the ovary.

In his experiments, he not only employed sulphate of magnesia, but also other salts, particularly the sulphates of soda and potash, sulphate of alumina and potash, chloride of calcium and chloride of sodium. The fluids employed were principally derived from the thoracic and abdominal cavities. The author arrived at the following conclusions:—

1. Albumen containing abundance of alkali is separated from its solutions by the above-mentioned salts. Robin and Verdeil, only experimenting with albumen, alkali and sulphate of magnesia, correctly indicate the magnesian precipitate produced by this mixture, but did not recognize the simultaneous separation of the albumen, which may be rendered more distinct by the employment of more soluble salts.

2. Solutions of albumen, very rich in salts, may be precipitated both in large and small quantities by the addition of free alkali. This difference however is observed, that when chloride of sodium is present this takes place immediately, but with sulphate of soda only on the application of a higher temperature.

3. The precipitability of the albumen under these circumstances depends essentially upon the intensity of the action of alkali. Very strong action of the alkali enables the albumen to separate in an insoluble form, and in this way a sort of gelatinous mass may be produced which is insoluble in water and alkalies, and under certain circumstances even in acids. The weak and short action of alkalies only produces a slight tendency to separation in the albumen, and the separated albumen is again soluble in water. But if the action, although weak, be continued, and especially if it be assisted by heat, the separation is much promoted, and the solution of the separated albumen in water becomes more difficult.

4. Alkaline albuminate, if not identical with common albumen,

must be regarded as a modification very nearly allied to this. The solution of the separated albumen always presents the greatest similarity with solution of ordinary albumen. It is possible, nevertheless, that, as was supposed by Panum to be the case with his acid albumen, certain splittings of the base may take place, but these may only have a material influence when insoluble precipitates are formed.

5. Alkaline albuminate is especially distinguished from ordinary albumen by the greater facility with which the water can be extracted from it. Hence arises the well-known phenomenon of the readiness with which the so-called caseine membrane is formed upon alkaline solutions of albumen during evaporation.

6. Alkaline albuminate occurs in greater quantity in the effused fluids, and probably in the pancreatic juice, than in the blood. The animal tissues are evidently much more readily permeated by it than by ordinary albumen, just as fat in the presence of alkali passes much more readily through animal membranes.—Liebig's *Annalen*, xci. p. 334.

On prepared Catechu. By Dr. J. J. POHL.

Under the name "prepared catechu for dyers and printers," a sort of catechu is sold, at a tolerably high price, which is said to possess great advantages over the ordinary commercial articles in respect of productiveness, and of the bright brown shades which are obtained with it. The prepared catechu exhibits in its fracture a darker and more fiery brown colour than the ordinary kind; it contains no foreign constituents of the plant, and the appearance alone shows that it has been exposed to a heat sufficient at least to soften it. On calcination it gave only 1.5 per cent. ash, which contained alumina, potash, and oxide of chromium as bases. The amount of the last substance, as well as the appearance, and the comparatively small amount of ash of the prepared catechu (for ordinary catechu gives from 7 to 12 per cent.), gave the hint to the preparation of a product quite equal to the sample.

Commercial catechu is melted in a water-bath, and kept in this condition for about an hour. Sand, earth, &c., settle for the most part to the bottom, and the purified catechu can be taken off from the surface. To free it from the still adhering leaves, sticks, &c., it is pressed while thick, melted through a sieve, which must not be too fine. The catechu is now brought into a clean vessel on the water-bath, kept at about the temperature of boiling water, and 0.75 per cent. of finely powdered bichromate of potash mixed in. The chrome-salt must be heated to about 212° F. for half an hour, with continual stirring; the mass is then allowed to cool, and formed into pieces of any form.

Dyeing experiments with the catechu prepared in this way gave in every respect the same results as those with the sample.

Since the ashes of the "prepared catechu" contain considerable quantities of alumina, I tried a mixture of potash alum with the bichromate of potash; but experiments with the catechu thus pre-

pared gave colours paler than those obtained with bichromate of potash alone.—*Sitzungsber. d. Kais. Akademie d. Wissensch.*, vol. xii.

On the Composition of Sugar of Milk, and its Behaviour with Oxide of Copper. By G. STÄEDELER and W. KRAUSE.

The formula adopted for anhydrous sugar of milk is $C^{12}H^{10}O^{10}$, for the crystallized, $C^{12}H^{10}O^{10} + 2Aq$. According to Berzelius's experiments, the latter, when heated above $212^{\circ}F$., loses 11.9 per cent. of water, a loss of 2 per cent. more than agrees with the formula $C^{12}H^{10}O^{10} + 2Aq$. Some chemists have therefore proposed the formulæ $C^{24}H^{19}O^{19} + 5Aq$ and $C^{10}H^8O^8 + 2Aq$ for the crystallized sugar. Both these formulæ agree better with the amount of water found than that usually adopted; nevertheless there is good reason to doubt their correctness, and the authors have on this account submitted sugar of milk to a new analysis.

Commercial sugar of milk was purified by repeated recrystallization from its solution in water, and the crystals dried in the air and over chloride of calcium were analysed. The results thus obtained (I. and II.) agreed very exactly with those of Liebig's analyses; but the authors purified the sugar still more by repeatedly precipitating it with alcohol from its concentrated watery solution. In this manner they got rid of a small quantity of lactate of lime, which adhered to it very pertinaciously; it then gave the result (III.):—

	I.	II.	Liebig.	III.		
Carbon.....	39.56	39.80	39.50	40.07	1=6	40.00
Hydrogen ..	6.73	6.65	6.74	6.70	1 1	6.67
Oxygen	53.71	53.55	53.76	53.23	1 8	53.33

Air-dried sugar of milk undergoes no change of weight either over chloride of calcium or at $212^{\circ}F$. Towards $266^{\circ}F$. some water is given off; between 284° and $302^{\circ}F$. the pounded crystals run together a little, but without acquiring colour. Decomposition begins about $320^{\circ}F$.; the sugar becomes brown, and evolves an odour of caramel.

The results of the following analyses lead to the formula $C^{12}H^{11}O^{11}$. In the analyses I. and II. the sugar was dried at $284^{\circ}F$.; in III. at $311^{\circ}F$.:—

	I.	II.	III.		
Carbon	42.05	41.97	41.83	12=72	42.11
Hydrogen.....	6.49	6.59	6.44	11 11	6.43
Oxygen.....	51.46	51.44	51.73	11 88	51.46

A continued heat is necessary for the expulsion of the water; it is driven off with the greatest rapidity between 284° and $293^{\circ}F$. The loss in four determinations was found to be,—

4.97 4.96 5.07 5.3,

or on the average 5.08 per cent. The composition of the crystal-

lized sugar of milk is therefore expressible by the formula $C^{12}H^{11}O^{11} + Aq$, which requires a loss of 5 per cent. of water.

When the anhydrous sugar of milk is exposed to moisture, it gradually recovers its water of crystallization; if water be poured over it, it is immediately converted into a solid mass.

According to these facts, anhydrous sugar of milk is isomeric with cane-sugar, and the crystalline form with anhydrous grape-sugar.

As cane-sugar and grape-sugar combine with chloride of sodium to form compounds, the authors tried to produce a corresponding compound with sugar of milk. They dissolved the sugar and salt in the equivalent proportions 2 : 1, in boiling water, and allowed the solution to evaporate spontaneously. The crystals which first separated proved to be pure sugar of milk; the following crystallizations consisted principally of chloride of sodium. No compound was obtained.

Sugar of milk, heated with peroxide of copper in an alkaline solution, reduces it to the state of protoxide with the same facility as grape-sugar, and this reaction is employed in the quantitative determination of sugar of milk. As test-fluids, solutions of sulphate of copper, tartrate of potash, and potash in various proportions, have been recommended; these all, however, as has already been observed, may often lead to erroneous results. The tartaric acid in these solutions undergoes a gradual decomposition, and then causes the separation of protoxide of copper during the boiling. If such a solution be exposed to the light of the sun for a few hours, the separation of protoxide of copper often commences without any application of heat. In consequence of this ready decomposability, it is better to employ free tartaric acid instead of tartrate of potash, and to prepare the mixture only a short time before it is wanted. The authors have endeavoured to determine the most favourable proportions with which to produce complete decomposition, and to ascertain the errors which may result from deviations from the proportions found.

1. A fresh-prepared solution of tartaric acid, boiled with an alkaline solution of oxide of copper, exerts no reducing action upon it. A solution of tartaric acid that has been long kept, on the contrary, induces reduction. The more diluted it is, the more rapidly does the decomposition take place.

2. To make peroxide of copper soluble in potash, 1 equiv. of tartaric acid ($2HO, C^8H^4O^{10}$) is required for 2 equivs. of the peroxide. If such a solution be boiled with an excess of potash, black oxide is separated. It is only when 3 equivs. of tartaric acid are present with 2 equivs. of peroxide of copper, that the solution remains clear with continued boiling. The next day however there is usually a deposit of bright red protoxide of copper, the formation of which must be ascribed to a decomposition of the tartaric acid by the potash.

3. If a solution of 2 equivs. of peroxide of copper and 3 equivs. of tartaric acid be mixed with 8 equivs. of potash (so that all the

acid may be combined with potash), a neutral fluid is obtained, which does not become turbid when boiled either by itself or with the addition of sugar of milk.

4. If the solution mixed with sugar contains 1 equiv. of free potash to 1 equiv. of peroxide of copper, turbidity is produced at about 140° F., and a yellowish precipitate gradually makes its appearance, which after long boiling becomes of a dingy orange colour. If the solution contains 1 equiv. of sugar of milk to 8 equivs. of peroxide of copper, a filtrate containing copper will be obtained after the boiling; but if the solution contains only 7 equivs. of the oxide, the filtrate is yellowish and contains undecomposed sugar. In both cases the fluid retains its alkaline reaction.

5. A solution containing 2 equivs. of free potash to 1 equiv. of peroxide of copper behaves in an exactly similar manner; but if it contains 3 equivs. of free potash, boiling immediately produces a beautiful red, heavy precipitate, which soon settles.

6. With these proportions it requires exactly 1 equiv. of sugar of milk for the reduction of 7 equivs. of peroxide of copper. If the quantity of potash be doubled, no important variation is observable.

7. A solution containing only sugar of milk with peroxide of copper is rendered permanently clear by potash only when 2 equivs. of sugar of milk are present to 5 equivs. of the oxide. The solution deposits no protoxide of copper when left standing for days, but reduction takes place immediately it is heated.

It appears therefore from these experiments, that 2 equivalents of sugar of milk are required for the reduction of 14 equivs. of peroxide of copper, but that this proportion only succeeds when the solution contains at least 3 equivs. of free potash to each equivalent of peroxide of copper. It is only in this case that pure protoxide of copper is formed, and the products of the decomposition of the sugar are not able to saturate the potash, even when its quantity is equivalent to that of the peroxide of copper. It appears also that the reaction remains the same even with a considerable excess of potash, but that important variations may occur when too little potash, or a decomposed solution of tartaric acid is employed. If protoxide of copper does not separate from the solution whilst boiling, but only after long standing, this does not arise from decomposition of the sugar, but from a decomposition of the tartaric acid by the potash. According to the sixth and seventh experiments, the equivalent of sugar of milk appears to be twice as high as the authors previously supposed.

The authors prepared their test-fluid by dissolving 10 grms. of pure copper wire in about 50 cub. centims. of concentrated muriatic and a little nitric acid in a retort, and boiling the solution until no more red fumes were produced. The excess of acid was got rid of by careful additions of potash, and the cold solution was diluted to 1000 cub. centims. Metallic copper is preferable to sulphate of copper, as the commercial sulphate is too frequently contaminated with iron. 10 cub. centims. of the solution contain 0.1 gm. of metallic copper, or 0.1252 gm. of peroxide of copper.

The solution of tartaric acid contains 15 grms. of acid in 40 cub. centims.; the potash solution contains 150 grms. of commercial hydrate of potash in 1000 cub. centims.; the potash must not contain more than about 10 per cent. of water separable by fusion.

These solutions are kept in cylindrical vessels with perforated corks, through which pipettes are passed. The pipettes must allow 10 cub. centims. of the copper solution, 10 cub. centims. of potash, and 2 cub. centims. of tartaric acid to flow out.

Before every experiment, these three fluids are mixed in the proportions just mentioned; the tartaric acid should follow the copper. If the mixture, diluted with an equal volume of water, does not become turbid on boiling, the saccharine solution to be tested may be added at once; otherwise the solution of tartaric acid must be renewed.

With these proportions, 0.0811 grm. of sugar of milk ($C^{12}H^{11}O^{11} + Aq$) are required for the reduction of the peroxide of copper. Numerous comparative experiments have given very concordant results when the saccharine solution to be tested was added in nearly the proper quantity, which may be ascertained in a few minutes by a preliminary experiment.

For ascertaining the amount of sugar in milk, 20 grms. are heated in a porcelain dish; the caseine is coagulated by a few drops of acetic acid, the filtrate slightly supersaturated with potash, and then diluted to 500 cub. centims. As a general rule, 40 cub. centims. of this fluid will be required for the decoloration of the copper solution.—*Mittheil. der Naturf. Gesellsch. in Zürich*, 1854, p. 473.

Analysis of the Tubers of the Chinese Potato (Dioscorea Batatas), cultivated near Paris during the year 1854. By E. FREMY.

The tubers analysed had the following composition:—

Water	79.3		
Solid matters	20.7	{ Starch	16.0
		{ Cellulose	1.0
		{ Mineral salts	1.1
		{ Albuminous matter	1.5
		{ Fatty bodies, sugar, soluble principles	1.1
	100.0		20.7

M. Boussingault had made a previous analysis of tubers grown at the Museum, and M. Payen of tubers from Algeria. The following are the results of these analyses:—

	Cultivated at the Museum.	Cultivated in Algeria.
Starch and mucilaginous substance	13.1	16.76
Albumen and other azotized matters	2.4	2.54
Fatty matters	0.2	0.30
Cellulose	0.4	1.45
Mineral salts	1.3	1.90
Water	82.6	77.05

By comparing these results with those of the analysis already given, it will be seen that the plants cultivated in France are actually approaching those grown in Algeria. The proximate principles of which the tubers are composed are to a great extent the same as those existing in the potato.

The Chinese potato only contains 16 per cent. of starch, whilst the potato may furnish 20 per cent.; the former however possesses a very remarkable azotized principle, which is not met with in the potato, and which may exercise a favourable influence upon the use of this valuable tuber. The mucilaginous principle which gives its unctuous properties to the juice of the *Dioscorea Batatas*, and which causes the pasty consistence assumed by this tuber when cooked, differs in its general properties from the gummy vegetable substances, and approaches albumen, being azotized and coagulable by heat.

This body must not be confounded with that which is often designated as *vegetable albumen*; it does not coagulate until after long boiling, and remains in great part in a soluble state in tubers which have been boiled or dried, even at a tolerably high temperature. Thus, the Chinese potato, when cut into thin slices and dried on a stove, furnishes a product which may be reduced to powder, and which when treated with water forms a paste resembling in its plasticity that produced by wheat-flour.—*Comptes Rendus*, Jan. 15, 1855, p. 128.

Further Researches on Bismuth. By R. SCHNEIDER.

The author has prepared compounds of bismuth with chlorine and sulphur. The methods employed for this purpose may probably be applied to the production of similar compounds of other metals. They are as follows:—

1. An intimate mixture of 8 to 10 parts of ammonio-chloride of bismuth ($2\text{NH}^4\text{Cl}$, BiCl^3) and 1 part of sulphur is heated in a retort until the mass begins to boil gently, when it is kept in this state until it acquires an intense brown colour. It is then allowed to cool, the residue is pulverized, and treated repeatedly with very dilute muriatic acid; in this manner the chloride of bismuth, which constitutes the greater part of the mass, is extracted, leaving an aggregation of acicular crystals, which are insoluble in very dilute muriatic acid. After sufficient washing and purification, these are a double compound of chloride and sulphuret of bismuth, BiCl^3 , 2BiS^3 . The gases evolved during the formation of this salt appear to be principally muriatic acid and nitrogen; and the formation of the crystals seems to take place at the cost of the ammonium, which gives a portion of its hydrogen to the sulphur to form sulphuretted hydrogen.

2. Ammonio-chloride of bismuth is heated to 482° – 572° F. in a retort, and sulphuretted hydrogen is passed over it. As soon as the mass has become brown by long action, the heat is raised to fusion. On cooling, the retort contains a cake of salt, which is treated in

the manner above described: It contains a larger quantity of crystals than the preceding. The reaction in this case is,—



3. Ammonio-chloride of bismuth is fused in a wide-mouthed flask; tersulphuret of bismuth, prepared either in the dry or humid way, is then put in until the mass acquires an intense brown colour. After cooling, the process is as above described.

The new compound of the sulpho-basic chloride of bismuth has, as already stated, the composition $\text{BiCl}_3, 2\text{BiS}^3$, and therefore represents the basic oxychloride of bismuth, $\text{BiCl}_3, 2\text{BiO}^3$. It forms small acicular crystals, with a beautiful metallic lustre and dark bluish-gray colour. The powder is tile-red, appearing ruby-red under the microscope by transmitted light. When heated in the air, sulphurous acid is evolved, and the residue is of a yellowish-white colour, consisting of basic chloride and basic sulphate of bismuth. When heated in a current of carbonic acid gas, the chloride of bismuth is evolved, and sulphuret of bismuth remains. Heated in hydrogen, a little chloride of bismuth goes off at first, then muriatic acid and sulphuret of bismuth, until the bismuth is reduced to the state of metal, retaining a little sulphur and chlorine.

Water and dilute acids scarcely attack the compound; concentrated muriatic acid dissolves it with evolution of sulphuretted hydrogen. Concentrated nitric acid oxidizes it immediately. Potash extracts all its chlorine, leaving an oxysulphuret. Its analyses gave,—

Bismuth	75.25	75.43	75.63	3 =	7800	75.37
Chlorine	12.13	13.03	13.01	3	1350	13.04
Sulphur	11.54	10.73	11.85	6	1200	11.59

The compound, $\text{BiCl}_3, 2\text{BiS}^3$, here described is also produced when tersulphuret of antimony is added to fusing ammonio-chloride of bismuth. The antimony is dispelled as chloride of antimony. —Poggendorff's *Annalen*, xciii. p. 464.

On the Compounds of Arsenious Acid with Iodide of Potassium.

By E. HARMS.

Emmet has stated that a solution of arsenite of potash, mixed with sufficient acetic acid to prevent reddening of turmeric-paper, gives rise to a pulverulent precipitate of the composition $\text{KI}, 3\text{AsO}^3$, on the addition of iodide of potassium. The author has tested this statement, and found that this salt contains water, which is not dispelled at 302°F . The quantity of potassium found amounted to 8.21.

In these experiments the author has also discovered two other salts of the same kind. One of these is produced when arsenite of potash is employed without neutralization by acetic acid, the precipitate formed on the addition of iodide of potassium dissolved in boiling water, the solution mixed with 3 or 4 vols. of hot alcohol, and then treated with carbonic acid gas until a film of salt begins

to be formed upon the sides of the vessel, and upon the tube through which the gas is passed. A syrupous fluid separates, containing much carbonic acid with iodine and arsenious acid. If the alcoholic solution be then further evaporated, a finely crystalline compound is obtained, with the composition $KI + 3(KO \cdot HO, AsO^3)$. Its analysis gave,—

KI	26.06	25.98	1	26.32
AsO ³	46.91	46.87	3	47.01
KO	21.35	21.15	3	22.39
HO	5.43	4.67	3	4.28

The 3 equivs. of water are not driven off at 212° F., and even at 526° F. the water was not expelled.

The salt is readily soluble in water and alcohol. The hot saturated solution deposits the following salt on cooling, in wartlike masses, in which no appearance of crystallization can be detected even under the microscope.

With the salts of the alkaline earths, earths and metallic oxides, this compound behaves generally like a mixture of iodide of potassium and arsenite of potash. Concentrated sulphuric acid throws down a red or yellowish-red precipitate of iodide of arsenic. Dilute sulphuric acid, and all other acids, decompose the compound. If a current of carbonic acid be passed through the hot saturated solution, a white pulverulent salt separates, the analysis of which led to the formula $KI, HO + 3AsO^3$: ~~+ KO~~ *— KI, HO + 10.0.0³ + 2 AsO³*

	Found.		Calculated.
KI	31.61	31.51	32.03
AsO ³	57.67	57.43	57.17
KO	8.43	..	9.07
HO	..	..	1.73

This salt has an alkaline reaction, and when heated evolves an abundance of arsenious acid with aqueous vapour and arsenic.—Liebig's *Annalen*, xci. p. 371.

✓ *On the Presence of Allantoin in the Urine during obstructed Respiration.* By F. T. FRERICHS and G. STÆDELER.

The authors tested Reynoso's statement, that in cases of continued interrupted respiration sugar was found in the urine. Under such circumstances the authors only found doubtful indications of sugar, but detected the presence of allantoin in some cases.—Müller's *Archiv*, 1854, p. 393.

ANALYTICAL CHEMISTRY.

Volumetric Determination of Copper. By C. MOHR.

THE author's method is founded upon the well-known fact, that salts of peroxide of copper are precipitated by metallic iron, the latter being converted into protoxide. The quantity of the protosalt of iron is determined by means of permanganate of potash.

The solution of the copper salt is put with a few drops of muriatic acid and about one-fourth of pure chloride of sodium into a stoppered bottle; a quantity of soft iron wire is then introduced. The reduction immediately commences, and should be assisted by a heat of 89° – 100° F. All the copper is separated in the metallic form in an hour or two, when no trace of copper can be detected in the solution by sulphuretted hydrogen. The following precautions must be observed:—The solution must not be too acid, as in that case an excess of iron is dissolved, and the heat applied must not be too strong, as this causes the separation of a basic persalt of iron in the form of a flocculent precipitate, which has no action upon the permanganate of potash. When the reduction is completed, which may be known by the clearness of the fluid, a protosalt of iron has taken the place of the persalt of copper, according to the formula $\text{CuO} + \text{SO}^3 + \text{Fe} = \text{FeO} + \text{SO}^3 + \text{Cu}$. The fluid is then diluted to 300 or 500 cub. centims. with the separated pulverulent copper; of this, 50 cub. centims. are drawn off by the pipette, and treated with permanganate of potash.

The following are some analyses performed in this manner:—

1.120 grm. of crystallized sulphate of copper was treated as above. The fluid was diluted to 300 cub. centims.; 50 cub. centims. of this required 5 cub. centims. of a solution of permanganate of potash = 30 cub. centims. for the whole quantity. 60 cub. centims. of this solution represented $\frac{1}{2}$ grm. of iron.

The metallic iron indicated by the 30 cub. centims. was therefore 0.25 grm.; we thus get the following equation:—

$$\frac{0.25 \times 125}{28} = 1.116.$$

1 grm. of sulphate of copper required 28.2 cub. centims. of a solution of the permanganate, of which 29.9 cub. centims. = $\frac{1}{4}$ grm. of iron. This gives 1.004 grm. instead of 1 grm.

1.4627 grm. of sulphate of copper took 44.1 cub. centims. of a solution, of which 33.5 cub. centims. = $\frac{1}{4}$ grm. iron. This gives 1.468 grm.

Pure red copper wire was treated in the same manner. It was dissolved in nitric acid; the nitric acid was destroyed by boiling with muriatic acid, and the solution considerably evaporated. The excess of acid was got rid of by carbonate of soda until there was only a slight acid reaction; this furnished the necessary quantity of chloride of sodium.

0.5 grm. of copper wire required 58.8 cub. centims. of a solution of permanganate of potash, of which 33.5 cub. centims. = $\frac{1}{4}$ grm. of iron. Result 0.5001, instead of 0.5.

0.5 grm. of the same wire gave 0.501 grm.

The analysis of brass may be effected in the same way, as the zinc has no injurious action.

1. 0.6625 grm. of brass wire was employed. The entire fluid after reduction required 49.8 cub. centims. of solution (30 cub. centims. = 0.25 grm. of iron). This gives the quantity of copper in the brass at 71.52 per cent.

2. 0.9632 grm. of the same wire gave 71.30 per cent. of copper.

With many other alloys the preliminary operations required render the process very long; thus it is necessary to separate the oxides of the heavy metals, and afterwards to destroy the nitric acid by evaporating the solution and adding muriatic acid. Those metals which are nearly allied chemically to iron, such as zinc, nickel and manganese, have not the smallest influence upon the reduction, and may be in solution with the oxide of copper in the form of oxides. Peroxide of iron has an injurious effect.

The author remarks that the separated cementation-copper dissolves gradually in dilute sulphuric and muriatic acids, deriving oxygen from the sulphuric acid. The copper was washed and mixed with a large quantity of distilled water; a few drops of concentrated sulphuric acid were then added. In ten minutes the fluid exhibited a distinct reaction of copper with sulphuretted hydrogen, and in an hour the sulphuret of copper produced by this reagent rendered the fluid opaque. The formation of sulphurous acid was proved by Löwenthal's test. This phenomenon is probably due to the large surface of the metallic copper.

Kerl has proposed to determine the weight of copper separated by means of metallic iron. His process has the advantage of being applicable to a larger series of compounds and alloys than the present method, but the difficulty of separating the metallic copper from the iron and the readiness with which it is oxidized are no small drawbacks.—Liebig's *Annalen*, xcii. p. 97.

Process for the Separation of Copper and Zinc.

By M. HAUTEFEUILLE.

One gramme of the alloy is dissolved in nitric acid; the liquid is concentrated and treated with liquid ammonia; by this means tin, lead, antimony, and iron would be separated if the alloy contained them. Acetic acid is then added in excess with a plate of pure lead, and the whole is kept boiling for two hours, when the liquid is decolorized and the copper precipitated in the metallic state. It is filtered, dried, ignited and weighed. After this weighing, the oxide of copper is dissolved in nitric acid; an excess of ammonia then shows whether it retains any traces of lead or antimony, which are deducted from the original weight. Calculation gives the weight of copper. If the alloy contained arsenic, it must be removed by means of a known weight of litharge before the employment of the acetic acid and lead plate; without this precaution the copper would be contaminated by it.

The liquid separated from the copper contains the zinc, with the lead which was added; the latter is got rid of by sulphuric acid, which furnishes a sulphate, which may easily be washed even by decantation. The wash-waters are evaporated to a very small volume, when the last traces of lead are removed by ammonia.

After this last treatment, the liquid is sometimes of a greenish tinge, indicating traces of copper; it must then be made very acid,

and a few bubbles of sulphuretted hydrogen are passed through it so as to precipitate the copper entirely; the sulphuret is washed, reduced to the state of oxide by calcination, and the weight of this is added to that previously obtained.

Finally, the liquid only containing zinc and ammoniacal salts is treated with carbonate of soda, and evaporated to dryness; the residue with a little carbonate of soda is taken up in water and boiled; ebullition brings the whole of the zinc to the state of carbonate, which is heavy and easily washed; this is filtered, dried, calcined and weighed; the weight of oxide gives that of the zinc.—*Comptes Rendus*, Jan. 15, 1855, p. 137.

Reaction for Caffeine. By Prof. W. DELFFS.

If a solution of iodide of potassium and mercury (obtained by saturating iodide of potassium with red oxide of mercury) be added to a solution of caffeine, a precipitate is produced, which in a short time forms an aggregation of shining, white, acicular crystals. The other alkaloids,—cinchonine, cinchonidine, quinine, paricine, strychnine, leucine, morphine, codeine, papaverine, narcotine, delphinine, emetine, veratrine, atropine, bebeerine, aconitine, solanine, oxy-acanthine, piperine, nicotine and coniine,—also furnish precipitates with this reagent, even when diluted 60,000 times, but these remain amorphous.—*Neues Jahrb. für Pharm.*, ii. p. 31.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Process for Tinning Metals. By MM. ROSELEUR and BOUCHER.

THE authors tin metals by decomposing solutions of certain double salts of tin, especially the phosphate, pyrophosphate, borate and sulphite, by means of the galvanic current. A solution for this purpose is obtained by dissolving 3 kilogrms. of pyrophosphate of potash and 500 grms. of protochloride of tin, in 200 litres of water. The temperature is raised to about 186° F.; and the bath may be kept saturated with tin by means of anodes of tin, by the action of the galvanic current. If it be observed that the bath does not deposit sufficient metal, a certain quantity of chloride of tin may be added to it; this at first forms a white precipitate, which however is again dissolved. A bath of this description, which had been constantly employed for a fortnight in tinning, required no addition of pyrophosphate, so that it might be expected that nothing of the kind would be necessary even for a much longer time. This process appears to be the only one proper for protecting zinc employed in roofing, in sugar moulds and kitchen utensils, from oxidation.

Cast iron tinned in this manner exhibits a fine silver-like appearance. The fluid for this purpose is prepared with—

Distilled water or rain-water	500 litres.
Pyrophosphate of soda	6 kilogrms.
Commercial tin-salt	1 ..
Dried and fused tin-salt	1½ ..

According to the strength of the alkaline reaction of the pyrophosphate of soda, which is not always of the same composition, the quantities of the fused and acid tin-salt must be varied. The bath must be kept at a temperature of 168°–186° F. The authors consider this composition to be the best, as its slight alkalinity precludes the disadvantage attending the use of an acid bath, which is favourable to oxidation, whilst it does not, like the strongly alkaline baths, deposit the tin of a bluish colour, nor require much washing to get rid of its taste.

At first the authors employed a separate galvanic battery, but it appears that this is only necessary in coating zinc with tin. For other metals it is sufficient to immerse these, previously well cleaned, in the bath, together with some pieces of zinc, when they will be covered with a dull coating of tin in the course of two or three hours. This may be polished with a wire-brush. If the coating of tin is required to be thick, the objects must be immersed several times. The bath may be used almost constantly; it is sufficient, before introducing new objects, to add 300 grms. of pyrophosphate of soda and the same quantity of the tin-salt. The pieces of zinc are gradually dissolved.

The bath employed in tinning zinc has the following composition:—

Distilled water or rain-water	600 litres.
Pyrophosphate of soda	5 kilogrms.
Dried and fused tin-salt	1 kilogram.

Le Technologist, 1854, p. 629.

Method of distinguishing between genuine and counterfeit black-dyed Cloths. By Dr. J. J. POHL.

In order to distinguish genuine black-dyed cloth from counterfeit dyed, the cloth is often boiled three or four minutes with water, to which about 2 per cent. each of alum and refined tartar have been added. Genuine dyed cloth is not changed by this operation, while counterfeit dyed goods assume a yellowish-red or cherry-red shade. This test is, on the one hand, uncertain in inexperienced hands, since by long boiling even genuine black colours pass into a dark brown-red; on the other, too indeterminate to allow indigo- and prussian blue-black to be distinguished from the chrome-black. This colour, reckoned latterly among the genuine blacks, is little permanent in sunlight, although it resists the action of alkalis and acids in a high degree.

The following test answers these requirements better. A small piece of the cloth to be tested is boiled for a minute with a saturated solution of oxalic acid, then washed with water, and dried. If the original colour has not at all suffered by this treatment, it was in

the highest degree genuine-coloured, that is, dyed black with indigo or prussian blue. If the colour is almost quite extracted, then it must have been counterfeit-dyed cloth; if there has been a change into yellow or reddish-brown, then the cloth can either have been counterfeit-dyed or dyed with chrome-black. To decide this, a fresh piece of the original cloth is boiled with water that contains about 8 per cent. chloride of lime; it is then washed and dried. If the colour remains unaltered, or changed into the darkest chestnut-brown, then the cloth can be considered as genuinely dyed in the wide sense of the word, that is, with chrome-black.

In any case the first test is preferable, and the test with chloride of lime is superfluous when oxalic acid alone produces no essential alteration.—*Sitzungsber. d. Kais. Akademie d. W.*, vol. xii.

PATENTS.

Patent granted to J. Tribelhorn and Dr. Bolley, for Improvements in the process of Bleaching Vegetable Fibrous Substances.

IN bleaching vegetable fibrous substances, as hitherto practised, those substances are subjected to boiling in caustic alkaline solutions. Now, by the use of certain metallic solutions, such as the oxide of tin mixed with caustic alkaline solutions, in the bleaching of vegetable fibrous substances, whether it be the bleaching of yarns or fabrics for the market, or the bleaching as a preparation for dyeing and printing, such boiling may be dispensed with.

The oxide of tin employed by the patentees is contained in a preparation known as "preparing salt," obtained by diluting 1 lb. of oxide of tin with water to 12° or 14° Twaddle, and adding thereto a solution of crystal of soda to the point of saturation, the quantity of crystal of soda required being about 1 lb. 14 oz. This preparing salt is used in various proportions and degrees of strength, according to the nature of the substance, and the degree of bleaching required. The treatment of the fibrous substance is as follows:—

First, as regards cotton fabrics to be bleached for the market. The fabrics are,—1st, steeped in lukewarm water for twelve hours; 2ndly, washed; 3rdly, steeped for two hours in a lixivium composed of 3 lbs. of preparing salt dissolved in 1 gallon of caustic soda of 68° Twaddle, and diluted to 1° Twaddle; 4thly, passed through the squeezers for the purpose of expressing and collecting the lixivium; 5thly, steeped for half an hour in vitriol diluted to 1° Twaddle; 6thly, washed; 7thly, steeped in a weak solution of bleaching powder, or passed through the bleaching liquor and laid on a heap for four hours; 8thly, steeped for three hours in vitriol diluted to 2½° Twaddle; 9thly, washed; 10thly, boiled in a solution of carbonate of soda of from 1½° to 1¾° Twaddle for three hours; 11thly, washed (N.B. the two last-mentioned operations are performed only in case the fabrics are to be bleached to the greatest perfection); 12thly, steeped in a solution of bleaching powder diluted to ½°

Twaddle for four hours; 13thly, steeped for three hours in vitriol diluted to 2° Twaddle; 14thly, washed.

Secondly, as regards cotton fabrics intended to be dyed or printed with spirit colours or steam colours. The treatment of the fabrics is the same as the foregoing; the lixivium, however, instead of being diluted to 1°, is diluted to 2° Twaddle.

Thirdly, as regards the bleaching of yarns (say 200 bundles). The yarns are,—1st, boiled in a solution of caustic soda of 2° Twaddle, in which is dissolved 1 lb. of preparing salt, for three hours; 2ndly, washed in the yarn-washing machine; 3rdly, steeped in a weak solution of bleaching powder for one hour; 4thly, washed; 5thly, boiled in water for half an hour; 6thly, steeped in a weak solution of bleaching powder for one hour; 7thly, washed; 8thly, steeped in vitriol, diluted to 1° Twaddle, and of 110° to 120° F., for half an hour; 9thly, washed; 10thly, steeped in a solution of soap of the temperature of 140° F. (4 oz. of soap to 1 gallon of water); 11thly, washed.

If the yarns are to be bleached without boiling in the lixivium, the operations, from the third to and including the ninth, have to be repeated in the above-named rotation till the desired degree of whiteness is attained.

The lixivium retains its properties for several months, care being taken every time after it has been used to add to it as much of a stronger solution as may be necessary to raise it again to the required strength.—Dated Dec. 19, 1853.

Patent granted to G. Robb, for Improvements in the Manufacture of Sulphuric Acid, Alkalies, and their Salts.

This invention relates to the production of sulphuric acid and sulphate of soda more economically than heretofore. In making sulphuric acid according to the improved process, the vapour of sulphurous acid is passed over peroxide of iron mingled with heated air; and the result of this process is sulphuric acid. Then, to produce sulphate of soda, the vapour of sulphurous acid is passed, along with heated air and steam, over a mixture of common salt and peroxide of iron.

Another branch of the invention relates to the production of sulphuret of sodium for the manufacture of carbonate of soda. This is accomplished by mixing the materials for the production of the sulphuret of sodium with sulphuret of calcium or soda waste; so that the sulphuret of sodium becomes workable on a large scale by being rendered innocuous in its effects upon the apparatus employed in the process.

In employing peroxide of iron for the production of sulphuric acid, it is preferred to use the pyrites cinder, resulting from the combustion of iron pyrites, as commonly produced in the manufacture of sulphuric acid at present. The pyrites cinder is first reduced to small pieces or to a state of powder; and in this condition it is placed in a furnace or kiln, such for example as is technically known in Scotland as a "draw-kiln." Round this kiln is ranged a set of

pyrites burners, such as are commonly used by sulphuric acid makers; and these burners are so arranged that all the products of combustion effected in them may pass into the kiln containing the pyrites powder. Common pyrites is deposited in these burners, and roasted in the ordinary manner, highly heated atmospheric air being at the same time admitted at the bottom of the pyrites kiln. By this arrangement, the vapour of sulphurous acid and the oxygen of the atmosphere are simultaneously brought into contact with the pyrites in the kiln (which pyrites is kept at a dull red heat), and the resultant combination is sulphuric acid.

In making sulphate of soda by passing the vapour of sulphurous acid over peroxide of iron and common salt, mixed together, and kept at a dull red heat, it is preferred to use the spent cinder from pyrites burners. Such spent pyrites cinder is reduced to a powder; and the common salt is mingled with such powder; and the compound is then placed in a kiln or chamber, as already described. The sulphurous acid generated in the manner above described is then passed through the heated materials, producing sulphate of soda. In manufacturing carbonate of soda, a sulphuret of sodium is first produced, and then decomposed by the action of carbonic acid. The common sulphate of soda is, in this process, decomposed by the action of suitable carbonaceous materials, in a kiln or common furnace. The ordinary materials for the production of sulphuret of sodium are mixed with sulphuret of calcium or soda waste. By this admixture, therefore, the sulphuret of sodium may be made on the large commercial scale, as that substance is by this treatment rendered innocuous in its effects upon the apparatus employed in the manufacture, both as regards the furnaces or operating chambers and the necessary iron tools of the workmen.—Dated March 26, 1853.

Patent granted to Alfred Trueman, for Improvements in the Manufacture of Sulphuric Acid when roasting Copper Ores, and also when burning Sulphur or Iron Pyrites.

This invention consists in passing the sulphurous acid, resulting from the roasting of copper ores, mixed with oxygen, atmospheric air, or any suitable matter containing oxygen, in contact with heated platinum, oxide of iron, or other substance, having in a heated state the property of causing oxygen to combine with sulphurous acid, so as to form sulphuric acid. And the invention also consists in the employment of platinum, oxide of iron, or other matter (having in a heated state the property of causing the combination of sulphurous acid and oxygen), diffused in the pores of pumice-stone, burnt clay, or other similar substance, for the purpose of converting a mixture of sulphurous acid and oxygen, atmospheric air, or other suitable matter containing oxygen, into sulphuric acid.—Sealed May 2, 1854.

[This invention, which the author calls his own, appears to be identical with that described by Prof. Wöhler at p. 156 of our volume for 1852.]

THE CHEMICAL GAZETTE.

No. CCXCVII.—March 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of the Protosalts of Iron upon Nitronaphthaline and Nitrobenzine, and on a new method of forming the artificial Organic Bases of Zinin. By A. BÉCHAMP.

I HAVE recently laid before the Academy of Sciences a note, in which I showed that by the reaction of protosalts of iron upon pyroxyline* and the analogous nitrated products derived from starch and gum, the original substances were very easily reproduced. The experiment with gun-cotton is particularly remarkable; all the nitrogen of the product is disengaged in the form of pure binoxide of nitrogen; the protoxide of iron at the same time becomes converted into peroxide and the cotton is regenerated, preserving its texture and its ordinary physical properties. These nitrated products consequently behave exactly like true nitrates.

If reducing substances of another nature, and especially sulphuretted hydrogen, be caused to act upon pyroxyline, a very different reaction takes place.

With nitrated substances derived from the hydrocarbons, such as nitronaphthaline and nitrobenzine, the action of protosalts of iron is also very different, and approaches that of sulphuretted hydrogen. All the nitrogen of the nitrated product remains combined with the residue of the elements of the hydrocarbon, and the corresponding organic base is produced. But whilst the production of aniline by means of sulphuretted hydrogen is very difficult, it is effected with remarkable facility by the protosalts of iron; and I think that of all the processes for the preparation of this base, none are so convenient and cheap as that which I propose.

The preparation of naphthalidame from nitronaphthaline by the new method is also very easy; and it appears that the process which I am about to describe may be usefully applied to the production of the artificial organic bases derived from the hydrocarbons.

Sulphate, oxalate, and protochloride of iron have no sensible action upon nitronaphthaline and nitrobenzine, the only bodies upon which I have operated hitherto. But an iron salt with a weak acid, the protacetate for example, is quickly acted upon; no gas is evolved, sesquioxide of iron is precipitated partly in the state of basic acetate, and naphthalidame or aniline is formed.

* Chem. Gaz., vol. xii. p. 11.

Nitronaphthaline—Naphthalidame.

If nitronaphthaline be put into an excess of a somewhat concentrated solution of protacetate of iron, scarcely any reaction takes place in the cold; but if the vessel containing the mixture be put into a bath heated to 212° F., the fusion of the nitronaphthaline has scarcely taken place before the reaction commences. A yellow precipitate is soon formed, and increases rapidly in quantity, whilst the peculiar fetid odour of naphthalidame is produced. The following equation explains the reaction that takes place:—



The following is the most convenient mode of operating in order to obtain naphthalidame. As too great an excess of the iron salt is unfavourable, it is necessary to ascertain, at least approximatively, the quantity of iron contained in the solution of the protacetate. For 100 grms. of nitronaphthaline, a solution of acetate containing 200 grms. of iron must be employed.

Naphthalidame speedily undergoes change by exposure to the air; it is therefore necessary to avoid contact with the air as much as possible, and for this purpose it is advisable to operate in a balloon furnished with a narrow tube. When the apparatus is placed in a bath of boiling water, the reaction is soon completed. With 20 grms. of nitronaphthaline a quarter of an hour is sufficient.

When the reaction is at an end, the free acetic acid and the excess of the iron salt must be removed. For this purpose the balloon is filled with boiling water and left to settle, which takes place very slowly. When the liquid has become clear, long needles of naphthalidame may often be observed and collected. The clear portion may be decanted and thrown away, as it only contains traces of the base. Boiling water is then poured over the deposit again, and the operations just described repeated. The precipitate is then put upon a filter. The filter and its contents are placed in a balloon, and exhausted by boiling alcohol of spec. grav. 0.845. The alcoholic fluids are concentrated by distillation as quickly as possible, and the residue in the retort treated with concentrated sulphuric acid. If the distillation has been carried far enough, the liquid sets into a mass of small nacreous crystals of sulphate of naphthalidame, which are but slightly soluble in cold alcohol. The crystals thus prepared have already acquired a slight red tinge from contact with the air; to purify them, they may be dissolved in boiling alcohol. But it appears that the red matter into which naphthalidame and its salts become converted by contact with the air, is more readily produced in presence of alcohol; for this reason the crystals may be collected on a filter, washed with a little cold alcohol, and dissolved in boiling water; on the cooling of this solution, the salt is obtained perfectly white and very well crystallized. To preserve the whiteness of the crystals, they must be rapidly dried *in vacuo*.

By treating a hot concentrated aqueous solution of this salt with ammonia, beautiful, white, flattened needles of naphthalidame are formed after some time. The naphthalidame thus obtained, its sul-

phate and muriate, present all the characters indicated by authors. Nevertheless, so as to leave no doubt as to the identity of the product obtained by the new method with that furnished by sulphuretted hydrogen, the amount of sulphuric acid contained in the sulphate was determined.

The salt analysed was perfectly crystallized in broad laminæ, and had scarcely any red tint; it was dried *in vacuo* at a temperature of 61° to 68° F.; it was dissolved in water acidulated with muriatic acid, in which solution took place readily with the aid of a slight elevation of temperature. Precipitated with chloride of barium,—

1. 0.544 grm. of sulphate furnished 0.336 sulphate of baryta; sulphuric acid, 21.218 per cent.

2. 0.569 grm. of sulphate gave 0.838 of sulphate of baryta; sulphuric acid, 20.407 per cent.

Average, 20.812 per cent. The formula $\text{SO}_3, \text{C}^{20} \text{H}^1 \text{N}$, HO requires 20.833 per cent.

Nitrobenzine—Aniline.

When nitrobenzine is poured into a solution of protacetate of iron, the latter is almost immediately reduced, an evident sign of the oxidation of the protoxide of iron; if the vessel containing the mixture be placed in a bath heated to 212° F., a yellow ochreous deposit is soon formed, and no gas is evolved. If the solution of acetate of iron contain 12 equivs. of that metal to every equivalent of nitrobenzine, the aromatic odour of the nitrated compound disappears, and gives place to the peculiar odour of acetate of aniline.

The reaction is the same as for naphthalidame, viz.



only that whilst the naphthalidame does not combine with the acetic acid, the aniline exists in the liquid in the state of acetate, which greatly facilitates its separation.

The following are two methods for the production of aniline:—

First Process.—Some acetate of iron, with a known strength in iron, is prepared. Theory indicates an acetate of iron containing 336 grms. of iron to 123 grms. of nitrobenzine. The employment of an acetate containing 3 parts of iron to 1 part of the nitrated compound, is most suitable.

The solution of acetate of iron and the nitrobenzine are put into a balloon, furnished with a tube leading into a cooled flask, which condenses a little acetate of aniline, which becomes volatilized. The balloon is heated in the water-bath; the conversion of 100 grms. of nitrobenzine takes an hour. After cooling, if the product of the reaction be too pasty, it must be suspended in water to filter it; after washing the residue with hot water, all the fluids are united in a retort, or in an ordinary plated alembic, in which nine-tenths of the liquid are distilled off. In the presence of aqueous vapour, both acetate of aniline and acetic acid distil over. It is necessary that the receiver should communicate with a cold flask, as under the

circumstances of the operation the acetate of aniline is so volatile, that without these precautions considerable quantities are lost.

The product of distillation is treated with 40 grms. of concentrated sulphuric acid to 100 grms. of nitrobenzene employed. It is again distilled, to condense the greater part of the acetic acid; when all this acid is driven off, the sulphate of aniline crystallizes on cooling in long silky needles. If there still remains much acetic acid in the residue, the sulphate of aniline unites into globular masses. By a second crystallization from alcohol, it is obtained in a state of perfect purity.

To obtain aniline itself, all that is necessary is to add a concentrated solution of caustic potash to the sulphate which remains in the retort, and to distil the mixture, after putting a good deal of broken glass into the retort.

To avoid the filtration in the preceding operation, it is sufficient to employ a *very concentrated* solution of the iron salt, and to effect the reduction of the nitrobenzene in a retort furnished with a well-cooled receiver. When the reaction is completed on the water-bath, the latter may be removed, and the distillation may be carried on by the open fire in presence of the precipitate. But during this distillation the liquid swells up, and to avoid accident a large retort must be employed, into which a great quantity of pounded glass has been introduced. The distillation is carried to dryness. This mode of operating has the advantage of getting rid of the preliminary filtration, and of giving fewer liquids to concentrate in presence of sulphuric acid; if the acetate of iron employed were very concentrated (to the point of crystallization), a distillate may be obtained so strongly charged that the acetate of aniline will separate from it in large drops. In this case the addition of caustic potash to the product is sufficient to separate the aniline which collects on the surface of the saturated liquid.

Second Process.—I have ascertained that by distilling a mixture of nitrobenzene, iron filings and acetic acid, aniline is formed, in accordance with the following equation:—



From this equation it is easy to see that for 123 grms. of nitrobenzene, 112 grms. of iron must be employed; a little more must be made use of, in order to make sure of the conversion of the whole of the nitrated compound. The preparation of aniline may therefore be modified as follows:—

1 part of nitrobenzene is put into a large retort with 1·2 part of bright iron filings and 1 part of concentrated commercial acetic acid free from mineral acid. The quantity of acetic acid should be sufficient to cover the iron filings completely. The reaction soon commences without the aid of heat; it becomes exceedingly brisk, the temperature rises, the liquid begins to boil, and all will be lost if the receiver be not well cooled. The results of the reaction are aniline, acetate of aniline, and a little nitrobenzene, which escapes the reaction. When the retort is cooled, the contents of the receiver

are poured into it. Heat is then applied to the apparatus, and the whole is distilled to dryness; the product, which passes up to the last moment, contains aniline, as may be proved by hypochlorite of lime, which produces the fine blue colour characteristic of this base.

In one operation I observed drops of a different appearance from that of acetate of aniline; I carefully separated the oily liquid that had passed, and having saturated it with dilute sulphuric acid, a light and very fluid liquid separated, which appeared to me to be benzene.

An excess of a solution of caustic potash is added to the distillate, when the hydrated aniline separates and rises to the surface, and may be removed and dehydrated in the usual manner. The base is obtained at once in sufficient purity. It sets into a mass with muriatic or sulphuric acid of moderate strength, and the salts obtained dissolve completely in water.

This method of producing aniline will allow of its preparation in the lecture-room, so as to show the instantaneous conversion of nitrobenzene into the state of a powerful base. The cheapness of this process is one of its greatest recommendations. In several experiments a quantity of aniline was obtained equal to three-fourths of the nitrobenzene employed; a kilogramme of nitrobenzene will furnish 750 grms. of aniline, so that with commercial benzene aniline may be obtained at a cost of about 20 francs per kilogramme. This base may thus be readily studied in other points of view than those of pure theory.

The aniline thus obtained is identical with that furnished by other methods, and possesses all the characters described by authors. Its odour is slightly vinous, as indicated by Hofmann. To prove with certainty that it was really aniline, the amount of sulphuric acid in its sulphate was determined:—

I. 0.407 grm. of sulphate of aniline gave 0.341 of sulphate of baryta; sulphuric acid, 28.740 per cent.

II. 0.325 of sulphate of aniline gave 0.274 of sulphate of baryta; sulphuric acid, 28.953 per cent.

III. 0.480 of sulphate of aniline gave 0.391 of sulphate of baryta; sulphuric acid, 27.97 per cent.

The average was 28.554 per cent.; calculation, according to the formula SO^3 , $\text{C}^{12}\text{H}^7\text{N}$, HO , requires 28.169 per cent.

Thus nitrobenzene, nitronaphthalene, and probably the nitric compounds of most of the hydrocarbons, are not reduced or regenerated by the protosalts of iron with strong acids; acetate of iron, and perhaps other iron salts with weak acids, cause the formation of an artificial organic base, corresponding with the nitrated hydrocarbon.

It will be interesting to observe how the protosalts of iron behave with the nitric derivatives of benzoic acid and its homologues, as well as with the higher nitric compounds of various hydrocarbons.

After succeeding in preparing aniline in such a simple manner, by the distillation of nitrobenzene with iron and acetic acid, I found

that this process is also applicable to the production of naphthalidame. As with aniline, this reaction is expressed by the following equation:—



1 part of nitronaphthaline is introduced into a retort furnished with a receiver, with 1·5 of iron filings and a sufficient quantity of ordinary commercial acetic acid to cover the mixture completely. The reaction does not commence in the cold, in consequence of the solid state of the nitronaphthaline; but when a few pieces of ignited charcoal are placed under the retort, the reaction begins as soon as the nitrated hydrocarbon fuses; the fire must then be removed quickly, as the reaction becomes as brisk as with nitrobenzene, and everything would pass over in consequence of the swelling of the mass, if the retort were not at least three times the volume of the mixture contained in it.

When the reaction begins to subside, the retort is placed on a sand-bath, plunging it up to the neck in the sand. If the distillation be properly managed, the acetic acid passes first of all, and if the heat be continued, the naphthalidame distils over at about 572° F., and condenses in the form of a yellowish oily stratum below the acetic acid, which must be left in the receiver, as it protects the base from the action of the air. To separate the acetic acid and purify the naphthalidame, it is sufficient to place the mixture in a retort, and distil it at a temperature of 259° F. The acetic acid first passes; the naphthalidame will distil over in its turn if the temperature be raised to 572° F., when it must be collected in a separate receiver. To preserve it without alteration, it must be poured into a bottle with a ground stopper, and solidified by refrigeration to 32° F. in a freezing mixture.—*Ann. de Chim. et de Phys.*, series 3, xlii. p. 186.

On Gum Mezgnite. By CAMPBELL MORFIT, M.D.*

Gum mezgnite, known synonymously as *muckeeet*, *mezgmeet*, and *musgnit*, and recently presented to public notice by Dr. G. G. Shumard, U.S.A., is said to be the product of a tree flourishing extensively in the high and dry regions of the plains of Western Texas, New Mexico, and the adjacent Indian territory. The facility with which it may be obtained in large quantities, and its very probable prospective value as an article of commerce, give it an interest that led me to a chemical examination which I have caused to be made in my laboratory by one of my students, Mr. Fred. W. Alexander.

It is a spontaneous semifluid exudation, concreting by exposure into tears and lumps of variable size and form. One sample, which was a part of that brought in by Dr. Shumard, and obtained directly from the U.S. Bureau of Indian Affairs, consisted of small irregular pieces and rounded balls about the size of a hazel-nut, semitransparent, and shading in colour from a lemon-white to a dark amber. When broken, the fractured faces were brilliant, and the gum was

* Communicated by the Author.

easily reduced under the pestle into a dull white powder. One of the balls was enveloped with an outer pellicle of gum about one-sixteenth of an inch in thickness.

The specific gravity of the gum was 1·5; but this determination may possibly admit of correction upon purer samples than were disposable for the experiment.

Its proximate composition was found to be,—

Water	11·640
Foreign matters.....	0·236
Bassorin.....	0·206
Arabin	84·967
Ash	3·000
	100·049

Cerasin was also sought, but not found. The ash was estimated by burning a given quantity in an atmosphere of oxygen, and weighing the residue.

The ultimate analysis, made also by effecting combustion of the carefully dried gum in oxygen gas, yielded, in two separate experiments, the following numbers:—

	I.	II.
Carbon	43·63	43·10
Hydrogen	6·11	6·50
Oxygen	47·26	47·40
Ash.....	3·00	3·00
	100·00	100·00

These proportions approximate very closely to those obtained from gum Senegal and Arabic, by Guerin and Mulder. The general appearance too of the gum is similar to that of gum Senegal and the dark inferior qualities of gum Arabic. In chemical properties also it is allied to them, being insoluble in absolute alcohol, partially soluble in common alcohol, and readily forming with hot or cold water a very adhesive mucilage. It is, in fine, a true gum, and promises, in its physical and chemical behaviour, much of the advantage expected by its discoverer as an economical substitute for gum Arabic or Senegal.

University of Maryland, Baltimore,
January 10, 1855.

On the Behaviour of Palm-oil when heated.
By Dr. J. J. POHL.

The melting-points of palm-oil, as observed by different chemists, present great discrepancies. This would lead at once to the conclusion, that the oil has not always the same constitution, a supposition which acquires still greater probability from the circumstance that the oil is obtained from the fruits of various palms, such as *Avoira elais*, and species of *Areca* and *Cocos*.

The author has determined a series of melting-points. Oil from various merchants, and of different age, exhibited very different melting-points. One sample (A), 94°.8 – 95°.2 F.; another (B) on an average 94°.1 F.; and a third (C) 76°.5 – 76°.9 F. Very old palm-oil, which had been kept at least two years, melted at 105°.8 – 106°.16 F.

The oil A, kept melted a considerable time in contact with the air at 190° – 199° F., exhibited a melting-point of 99°.5 F. The fat, purified by filtration whilst hot, was then exposed to a higher temperature. At 239° F. the fat employed began apparently to boil, probably in consequence of the evaporation of a small quantity of water which it might contain; this ceased at 368°.6 F. But even at 294° F., very acid, pungent, white vapours began to be formed (exhibiting no resemblance in odour to acroleine); these became very troublesome at 374° F., although the weight of the substance thus volatilized was inconsiderable. At 474°.8 F., boiling did not take place. The palm-oil then had a dark-brown appearance; but a portion of it, poured into cold water to cool it rapidly, no longer showed any trace of a yellowish-red colour; the palm-oil was bleached in this manner; and although still somewhat brownish, was quite as white as the best palm-oil bleached according to Payen's method. It had the consistence of hog's lard, an empyreumatic odour, the peculiar odour of palm-oil having entirely disappeared, and a waxlike taste. The portion of the heated palm-oil which had not been poured into water was still fluid after standing two hours at 72°.5 F., and the separation of a solid body only commenced in three hours. After nineteen hours a third part was still fluid, and a brownish-red oil flowed spontaneously from the fatty mass, amounting to about one twenty-fifth of the whole. In the course of sixty hours, even this oil solidified into a brownish-white mass. The bleaching of palm-oil therefore takes place under the above circumstances in a short time, as completely as by Payen's process in ten or twelve hours.

It was now to be ascertained whether the access of light and air was necessary for the bleaching; and to settle this point, palm-oil was heated in a covered vessel and in the dark to 475° F., and left to cool after exposure to this temperature for ten minutes. The palm-oil was, as before, completely bleached. At this high temperature therefore the destruction of the yellowish-red colouring matter is not effected either by the action of light, or by oxidation at the expense of the atmospheric oxygen.

To find the lowest temperature at which this rapid bleaching can be advantageously effected, palm-oil was heated in twenty-four minutes to 410° F., and kept at this temperature for six minutes; on cooling, it was certainly lighter in colour, but not perfectly bleached. Heated in fifteen minutes to 419° F., and kept at this temperature for fifteen minutes more, the palm-oil was lighter in colour than in the preceding case, but still not sufficiently bleached. When kept at 469°.4 F. for fifteen minutes, it appeared completely decolorized. Lastly, when palm-oil was heated in twelve minutes to 464° F., a

sample drawn at once still retained a yellow colour; but in five minutes it was colourless. From the above experiments it appears that when palm-oil is quickly heated to 464° F., and kept for a few minutes at this temperature, it is perfectly bleached without access of air or light. The author has not only tried this mode of bleaching on a small scale, but it has been carried out for three years in a manufactory. The heating of the palm-oil is effected as rapidly as possible in cast-iron pans; it is kept for ten minutes at a temperature of 464° F., and the bleaching is then completed. Ten or twelve hundredweights of palm-oil may be conveniently heated in one pan, which must however only be two-thirds filled, as the palm-oil expands greatly by the heat. It must be covered with a well-fitted cover, which prevents inconvenience from the above-mentioned acid fumes. The palm-oil acquires a purer white colour when operated upon on a large scale, than when treated in small quantities; it furnishes a very fine, solid, white soap. The empyreumatic odour which occurs immediately after the bleaching is lost after some time, and the original violet-like odour of the palm-oil again returns. The soap prepared from it has also a pleasant violet-like odour, as the empyreumatic smell entirely disappears during saponification. Palm-oil which is much contaminated with vegetable matters should be melted at a lower temperature before bleaching, so as to allow the impurities to settle. The best samples of palm-oil never contain more than from 0.3 to 1.0 per cent. of such impurities.

If palm-oil be heated to 572° F. with access of air, it begins to boil, and a strong odour of acroleine is perceptible. Distillation, carried on at 572° – 592° F., proceeds very slowly, as the vapours formed are heavy and readily condensable; but if ordinary steam be allowed to flow into the fatty mass heated to 572° F., the distillation takes place very quickly. At the commencement of boiling the palm-oil froths much, and easily passes over into the receiver; but in a few minutes this frothing ceases, and the distillation goes on without further disturbance. The author has effected the distillation of quantities of from 30 to 50 lbs. of palm-oil. If the fat be in contact with atmospheric air at the point of distillation, acroleine is formed with the mixture of fatty acids which passes over. The action of this substance upon the lachrymal glands and the organs of smell and respiration is terrible. The same odour is acquired under these circumstances by the products of distillation, and they cannot be freed from it even by boiling with water. But if care be taken that, when the palm-oil has reached the temperature of 572° F., all atmospheric air shall have been expelled from the apparatus by steam, not the smallest odour of acroleine makes its appearance during the distillation, which takes place without any trouble to the workman. At the end of the operation a blackish-brown fluid remains in the distilling vessel, which on cooling sets into a tough and elastic mass, and may be employed as an ingredient in the production of common soap, in the preparation of engine-grease, &c.

From good crude palm-oil purified by fusion, from 68 to 74·6 per cent. of fatty acids were obtained by distillation. The colour and consistence of the distillate is not the same at different periods of the operation. At first from 25 to 30 per cent. of perfectly colourless fatty acids come over rapidly; these, when solidified, form a solid mass; after this the products of distillation pass more slowly, always becoming more greasy on cooling, and more and more of a brownish colour. The empyreumatic odour of the fatty acids is lost in time, giving place to a waxy odour. If the colourless product of distillation be kept in the fused state for a considerable time, even at a low temperature, or repeatedly fused, it gradually acquires a darker colour, and at the same time becomes softer.

Determinations of the melting-points of the fatty acids obtained by distillation gave the following results:—

First Experiment.—The first half of the distilled fatty acids, which was of a slightly yellowish-white colour, was,—I. transparent at 105° F., and melted at 117°·5 F.; II. transparent at 104° F., and melted at 117°·5 F.

The second half of the distillate, of a strong brownish-white colour, was,—I. transparent at 101°·3 F., melted at 110°·7 F.; II. transparent at 101°·7 F., melted at 110°·9 F.

The second half of the distillate, after complete cold pressure, fusion with water to which 0·25 per cent. of oxalic acid had been added, and fining with white of egg, had a slightly brownish-white colour; it was,—I. transparent at 107°·4 F., fused at 121°·5 F.; II. transparent at 107°·8 F., fused at 120°·7 F.

II. is a mere repetition of the determination of the melting-point of the mass serving for the first experiment (I.).

Second Experiment.—The products of distillation were collected in five separate portions. The per-centage proportions, compared with the entire distillate, were for the first portion 1·21 per cent., 2·28 per cent., 3·17 per cent., 4·9 per cent., 5·25 per cent.

The determinations of the melting-points gave the following results:—Portion 1, transparent at 111°·9 F., fused at 124°·5 F.; 2, transparent at 103°·1 F., fused at 114°·4 F.; 3, transparent at 103°·1 F., fused at 113°·7 F.; 4, transparent at 103°·1 F., fused at 113°·7 F.; 5, transparent at 99°·1 F., fused at 109° F.

The coloured fatty acids obtained by distillation may easily be prepared colourless by recrystallization from alcohol. The author found the melting-points of several portions of such purified fatty acids to be,—

1st crystallization	137°·4 F.
2nd crystallization	140°·7 F.
3rd crystallization	138°·9 F.
4th crystallization	138°·5 F.

For comparison with the above determinations of the melting-points of the products of distillation of palm-oil, the author gives the following results obtained by him with fatty acids obtained by the

processes of Masse and Tribouillet, by treating palm-oil with sulphuric acid, and subsequent distillation with superheated steam.

The distillate of palm-oil, obtained in the year 1851 directly from the manufactory at Neuilly, and of a pure white colour, was,—I. transparent at $98^{\circ}5$ F., fused at $106^{\circ}9$ F.; II. transparent at $94^{\circ}1$ F., fused at $106^{\circ}5$ F.

The second portion of the distillate, obtained from the same manufactory, but pressed and of a dazzling white colour,—I. became transparent at $106^{\circ}7$ F., fused at $123^{\circ}1$ F.; II. became transparent at $108^{\circ}5$ F., fused at $120^{\circ}9$ F.; III. became transparent at $108^{\circ}5$ F., fused at $120^{\circ}5$ F. The second and third determinations were repetitions of the first with the same mass of fatty acids.

Palm-oil distillate, from the close of the operation, also from Neuilly, crystallized and pressed, also of a dazzling white colour,—I. became transparent at $109^{\circ}2$ F., fused at $120^{\circ}4$ F.; II. became transparent at $109^{\circ}4$ F., fused at $120^{\circ}4$ F.

After keeping for two years exposed to the light, the substances, which were originally pure white, acquired a somewhat brownish tinge.

Fatty acids, prepared in Vienna according to Tribouillet's method, as employed in August 1851 in the production of the Belvidere candles, and of a brownish-white colour, became transparent at $103^{\circ}1$ F., and fused at $118^{\circ}9$ F.

Fatty acids, afterwards prepared in Vienna, were pure white, like those produced in France, and their melting-points agreed pretty well with those of the latter.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xii. p. 80.

Note on the Conversion of Protoxide of Lead into Minium at the ordinary Temperature. By A. LEVOL.

The author found that some cupels, saturated with lead and copper (the former in the state of protoxide), which had been kept for several years in an imperfectly-closed jar in a damp place, had acquired a bright red tint in consequence of the conversion of the protoxide of lead into minium. This change had taken place not only at the surface of the cupels, but throughout their substance. In inquiring into the cause of this phænomenon, he endeavoured to solve the following questions:—

1. Has the oxide of copper anything to do with its production?
2. Has the substance of the cupel any influence, and if so, what is its mode of action, and is its action due to the phosphate of lime of which it is principally composed, or to the free lime which it contains?
3. Is water necessary for the production of the phænomenon? and does it act merely as a medium, or by its own decomposition as a direct oxidizing agent?

To solve these questions, pure lead was absorbed by cupels, which were then exposed to the air under the following conditions, and with the results indicated:—

1. Dry air, in diffused light.. no action.
2. Dry air, in the sun no action.
3. Dry air, in the dark no action.
4. Moist air, in the dark no action.
5. Moist air, in diffused light formation of minium.
6. Moist air, in the sun formation of minium more rapidly than in the preceding case.

These experiments show that the presence of oxide of copper is unnecessary, and that the agency of light and moisture is indispensable. The mode of action of the moist air and of the substance of the cupel remained to be determined; for this purpose the following experiments were made in moist air, with the results annexed:—

1. With pure protoxide of lead in powder.. no action.
2. With a mixture of equal parts of protoxide of lead and bone phosphate of lime previously deprived of free lime no action.
3. With a mixture of equal parts of protoxide of lead and caustic lime formation of minium.

The mixtures were exposed for several weeks to the direct rays of the sun.

To ascertain the mode of action of the moisture, a mixture of equal parts of protoxide of lead and caustic lime were put into a porcelain capsule, placed at the bottom of a narrow glass vessel, at the surface of a tolerably thick stratum of water; a stick of phosphorus, occupying the whole height of the vessel, was then introduced, and the vessel was hermetically closed. After the phosphorus had been in contact for several days with the confined air of the vessel, and the latter was supposed to be deprived of its oxygen, the apparatus was exposed to the sun, when the phosphorus soon melted, and sunk to the bottom of the water, so that the mixture was exposed to the light in a moist atmosphere deprived of oxygen. In about a month no minium was formed, so that the oxygen of the air is the oxidizing agent when the experiment is performed in contact with the air.

The author has only experimented with lime, but he entertains no doubt that other alkaline bases would have a similar action.—*Ann. de Chim. et de Phys.*, 3 sér., xlii. p. 196.

Thoughts on Solution and the Chemical Process. By T. S. HUNT.

By solution, as distinguished from fusion or volatilization, we understand in chemistry the production of a homogeneous liquid by the combination of two or more bodies, one of which must itself be in a liquid state, while the others may be liquid, solid or gaseous. The solvent action of acids and alkalies upon bodies insoluble in water is by all admitted to be chemical in its nature; but according to Leopold Gmelin, "mixtures of liquids, and solutions of solids in liquids (as of acids, alkalies, salts, oils, &c., in water and alcohol),

are by Berzelius, Mitscherlich, Dumas, and others of the most distinguished modern chemists, regarded as not chemical unless they take place in definite proportions." "Mitscherlich attributes such unions to *adhesion*, Dumas to a *solvent power* intermediate between cohesion and (chemical) affinity, and Berzelius refers them to a *modification of affinity*, while proper chemical combinations, according to him, result not from affinity, but from electrical attraction." (Gmelin's Handbuch, English ed. vol. i. p. 34.)

The learned author of the 'Handbook' objects to these views, that "they restrict the idea of a chemical compound within too narrow limits," and he elsewhere implies that the force which produces solution is a weak degree of chemical affinity. (*Id.* vol. i. p. 70.) The judicious Turner also speaks of ordinary solutions as instances of chemical union*; and Mr. J. J. Griffin has insisted upon the same view†. As these writers have not however sufficiently dwelt upon the important principle, rejected by so many names of authority, that *all solution is chemical union*, we propose to offer some considerations upon aqueous solution, and endeavour to show that the process presents all the phenomena of chemical combination,—first, in the fact that the resulting saturated solutions are perfectly homogeneous; secondly, in the condensation and more or less perfect identification of volume observed in the process‡ (some anhydrous salts dissolve in water without increasing its volume); thirdly, in the change of temperature which attends the process; thus oil of vitriol, hydrate of potash, and many anhydrous salts evolve heat when dissolved in water, while sal-ammoniac, nitre, and many hydrous salts produce cold by their solution; fourthly, in the change of colour which attends the solution of some salts, as the chlorides of nickel, cobalt and copper.

It must not be forgotten that the liquid state of these aqueous combinations is often an accident of temperature; alum and the rhombic phosphate of soda are liquids at 212° F., and bihydrated sulphuric acid is a crystalline solid below 46° F. The ease with which many of these compounds are destroyed by evaporation, and even by changes of temperature, is not to be urged as an objection to the chemical nature of the union. We need only compare the corresponding silver salts with the chloride and iodide of gold or the hydrochlorates of morphine and ammonia with those of caffeine and piperine, which lose their acid by a gentle heat, to learn how variable is the stability of admitted chemical compounds. Chemical affinity may be very feeble in degree.

According to Gay-Lussac, 1 part of oil of vitriol will absorb from air saturated with moisture 15 parts of water, or more than 80 equivs. Terchloride of arsenic requires 18 equivs. of water to dissolve it, and the saturated solution unites with as much more water, evolving

* Elements of Chemistry, 7th ed. p. 139.

† L., E., and D. Phil. Mag., series 3, vol. xxix. p. 299.

‡ See my paper, "Considerations on the Theory of Chemical Changes, &c.," L., E., and D. Phil. Mag. [4], v. 526; and Pharm. Centralblatt, Leipzig, 1853, 849.

heat and forming a stable solution*. According to the experiments of Mr. Griffin in the paper cited above, the condensation which takes place in the solution of the acid is still perceptible with 6000 equivs. of water to 1 of SO^3 . There appears however to be with many bodies a limit beyond which the affinity for water is satisfied, and the liquids being then mechanically mixed, gradually separate by reason of their difference in density, as is observed in dilute alcohol, and probably in some saline solutions† and metallic alloys.

Solution is a result of that tendency in nature which constantly leads to unity, condensation, identification. I have elsewhere, with Kant, defined chemical union to be interpenetration; but the conception is mechanical, and therefore fails to give an adequate idea. The definition of Hegel, that *the chemical process is an identification of the different, and a differentiation of the identical*‡, is however completely adequate. Chemical union involves an identification, not only of the volumes (interpenetration mechanically considered), but of the specific characters of the combining bodies, which are lost in those of the new species. Such is equally the case in aqueous solution, and we may say that all chemical union is nothing else than solution; the uniting species are, as it were, dissolved in each other, for solution is mutual.

Solution being then identification, the discussion as to whether metallic chlorides are changed into hydrochlorates when dissolved in water, is meaningless. Such a solution is a unity, in which we can no more assert the existence of the chloride or of water than of chlorine, hydrochloric acid, or a metallic oxide, although these and many others are conceivable results of its differentiation. If the solution be one of chloride of potassium, evaporation resolves it into water and the chloride; but if chloride of aluminium, it is decomposed by boiling into water, hydrochloric acid and alumina, or in the case of the magnesian salt, into hydrochloric acid and an oxy-chloride.

The precipitation of the sulphates of cerium, lanthanum, and lime from their solutions by heat, and of most other salts by cold, is chemical decomposition or differentiation. Dilution may also effect decomposition in solutions; we have already said that the combination of terchloride of arsenic, AsCl_3 , with 36HO is stable at ordinary temperatures, but a further addition of water causes the solution to divide into aqueous hydrochloric acid and crystalline oxide of arsenic. The precipitation of chloride of antimony and many

* Penny and Wallace, L., E., and D. Phil. Mag., Nov. 1852, p. 363.

† See Gmelin's Handbook, Eng. ed., vol. i. p. 111. Gmelin throws a doubt upon these experiments; but the satisfactory results obtained on a large scale, in applying this principle to the rectification of spirit of wine by a recently patented process, were communicated to the American Association for the Advancement of Science, at Washington, in May 1854, by Dr. L. D. Gale.

‡ Stallo's Philosophy of Nature, p. 453. See also p. 67, where Stallo insists upon the same view. To Hegel belongs the merit of having first among modern philosophers obtained a just conception of the nature of the chemical process, although in its application he was misled by the received terminology of the science.

salts of bismuth and mercury by water, is an analogous process. This decomposition of the solution of chloride of arsenic is an example of what is called double elective affinity (*attractio electiva duplex*), and is generally explained by saying, that the attraction of arsenic for oxygen, and that of chlorine for hydrogen, enable the chloride and water to decompose each other. But these elemental species do not exist in the solution, although they are possible results of its decomposition; and to explain the process in this manner is to ascribe it to the affinities of yet unformed species.

I have elsewhere asserted that double decomposition always involves union followed by division*, although we cannot in every case arrest the process at the first stage. Under some changed conditions of temperature and pressure, the decomposition may be the counterpart of the previous union, and thus reproduce the original species, as in the case of mercuric oxide, which is decomposed into mercury and oxygen at a temperature a little above that at which it was formed. When the division takes place in a sense different from the union, giving rise to new species, we have double decomposition. In the case of chloride of arsenic, the aqueous solution exhibits the first stage of the process. A similar condition of unstable union is observed in many other instances; thus binoxide of manganese gives with cold hydrochloric acid a brown solution, but the combination is by a gentle heat resolved into chlorine gas, and a rose-red solution of protochloride of manganese. So a mixture of equivalent parts of chloride of benzoyle and benzoate of soda combines at a temperature of 130° C. to form a limpid solution, and it is only on raising the temperature that the precipitation of sea-salt indicates the commencement of that decomposition which yields at the same time anhydrous benzoic acid†. It is only when looked upon as a momentary combination followed by a decomposition, that the theory of double decomposition becomes intelligible, and in accordance with known facts.

From the narrow limits of temperature which often include the two processes, and from the ease with which light, warmth, friction, and pressure excite the decomposition of such bodies as the chloride of nitrogen, the nitrite of ammonia, the oxides of chlorine, and the metallic fulminates, we may conceive that within still narrower limits, and under conditions as yet undefined, many bodies may exhibit affinities for each other, which are reversed by a very slight change of condition. In this way we may explain many of those obscure phænomena hitherto ascribed to *action by presence* or *catalysis*.—Silliman's *Journal*, January 1855.

On the Manufacture of Alcohol from Sawdust.

By M. ARNAULT.

The disease of the vine, and the consequent dearness of wine, has directed attention to different methods of obtaining alcohol without

* Considerations on the Theory of Chemical Changes, &c., cited above.

† Gerhardt, *Ann. de Ch. et de Phys.*, series 3, vol. xxxvii. p. 299.

the aid of the grape or the cereal grains, which last the French government protects, as their use diminishes the amount of food and raises prices. Recourse has been had to the juice of the beet, which has given rise to an extensive establishment under M. Leplay. But as this use of the beet is at the expense of the sugar, and would finally turn the sugar manufactories into distilleries, we now hear of the alcohol of Indian corn, alcohol of couch grass ("*chiendent*"), alcohol of asphodel, which have begun to be manufactured in the colony of Algiers. Quite recently, M. Arnault has applied to the same purpose the fact discovered by M. Braconnot of Nancy, and which consists in transforming wood into sugar by means of sulphuric acid. M. Arnault has observed that poplar wood gives the best results, affording 79 to 80 per cent. of sugar to be converted into alcohol. The wood is reduced to coarse sawdust, then dried at 100° C.; after cooling, sulphuric acid is added in small portions, taking care that the material does not become heated. It is well mixed, and after repose for twelve hours it is triturated until the mass, before almost dry, becomes quite liquid so as to run. This liquid, diluted with water, is made to boil; the acid is saturated with chalk, and the liquor after filtration is subjected to fermentation; when the alcohol is distilled off by the usual process.

The quantity of sulphuric acid employed should not be less than 110 parts for 100 by weight of the dry wood. The author hopes to diminish the quantity of acid, and is engaged at this time on this part of the process. We cannot say that the process will be economical.—Silliman's *Journal*, January 1855.

On the Pancreatic Secretion. By Dr. C. SCHMIDT.

In the examination of the pancreatic juice, made some years since by the author in conjunction with M. Bidder, the conclusion was arrived at, that it partly occasioned the conversion of the starch of the food into gum and sugar, and partly by taking a share in the intermediate intestinal circulation, caused the rapid movement of liquids within the body; but that the digestion of albuminous substances was effected by the gastric juice, that of fatty matters by the bile, and that neither was produced by the pancreatic juice. In these experiments, the authors procured the pancreatic secretion in drops of oily consistence and the aspect of white of egg, by means of a silver canula. As Drs. Weinmann and Ludwig of Zürich have since that time solved the problem of forming permanent pancreatic fistulæ in dogs, M. Schmidt has repeated his experiments, because by this method the pancreatic juice is obtained in larger quantity, and with different properties, forming a transparent liquid.

The pancreatic juice collected after the operation contains 10-11 per cent. of solids, 9-10 per cent. of which consist of organic matters (pancreatic diastase), and 0·8-0·9 per cent. of inorganic bases and salts; that from the permanent fistula contains 1·5-3·6 per cent. of solids, 1·5-2·3 per cent. being organic (pancreatic diastase, &c.), and 0·62-0·75 per cent. inorganic bases and salts; when the body

of the animal weighed 1 kilogram., from 0.1–0.2 gm. of the former, and from 3 to 5 grms. of the latter were obtained in an hour.

The pancreatic secretion obtained from a perfectly healed, permanent fistula, is clear, colourless, strongly alkaline, and of a faint soapy taste, without any particular odour; spec. grav. 1.010 to 1.011; it froths strongly when shaken, immediately converts starch-paste into gum and sugar at 99° F., and decomposes fatty matters; it becomes turbid at 158° F., and coagulates perfectly at 162° in white flakes. It is coagulated by alcohol and pyroxylic spirit; the coagulum (pancreatic diastase) redissolves in pure water, forming a clear solution, which decomposes starch-paste and butter like the original liquid. This fermentative power is destroyed by boiling, as also by sulphuric, nitric, muriatic, and metaphosphoric acids, and bichloride of mercury; these produce copious white precipitates, whilst acetic, sulphurous, and tribasic phosphoric acids, potash and ammonia, even when a few drops only are added, prevent the action, without producing turbidity or a precipitate. The two last, as also alkaline carbonates, added in large quantity, prevent the coagulation by heat. Perchloride of iron produces a bright blue flaky precipitate, iodine and hydriodic acid a rust-coloured, and chlorine and bromine yellow precipitates. In these cases, both the liquid and the precipitate have lost the fermentative power, whilst it is not in the least interfered with by salts of strychnine, salicine, cinchonine, or morphine, urea, hydrocyanic acid or bile. Acetate of lead produces a dense, white, flaky precipitate, soluble in excess of the precipitant. This solution, as well as the precipitate, acted upon starch. The gastric juice did not prevent the action of the pancreatic liquid. Solution of grape-sugar, mixed with and confined over mercury, remained unaltered. In three weeks, evolution of carbonic acid took place, but ceased in a few days, the liquid having acquired an acid reaction.

On cooling it below 32° F., before solidification took place, gelatinous coagula, resembling quince-mucilage, separated, which were less alkaline, and acted more powerfully upon starch than the liquid itself. The pancreatic juice, when dried in thin layers, forms a colourless transparent mass, resembling the mucus of the mouth, which swells in water and dissolves, forming a clear solution, the action upon starch remaining almost unchanged. If dried in thick layers, a great portion of it is decomposed.

According to the author's experiments, 1 kilogram. of an animal body (dog) yields in an hour,—

a. The absolute weight of the body being 8 kilograms., 5.03 grms., or 2.16 per cent.=0.106 gm. of solid matter.

b. The absolute weight of the body being 18 kilograms., 3.11 grms., or 1.99 per cent.=0.061 gm. of solid matter.

c. The absolute weight of the body being 26 kilograms., 2.99 grms., or 2.45 per cent.=0.73 gm. of solid matter.

Hence it is evident from these experiments, that the relative amount of secretion for the same genus of animal is directly proportional to the relative nutritional requirement.

The author's experiments show also, that 1 grm. of fresh pancreatic secretion, containing 0.021 grm. of anhydrous matter, this consisting of 0.014 grm. of organic substance (pancreatic ferment), 0.007 grm. of inorganic bases and salts, when digested at 99° F. for half an hour with excess of starch-paste, convert 4.672 grms. of anhydrous starch; so that 1 grm. of dried pancreatic diastase renders 333.7 grms. of the latter capable of being absorbed by the intestine under the above conditions. In the following analyses, three portions of 50 to 100 grms., collected at different periods, were used.

A. Clear colourless secretion; specific gravity *in vacuo* at 59° F. 1.0106.

42.426 grms. of the fresh secretion, dried at 230° F., left 0.985 grm.; this, heated to redness, gave 0.387 grm. of fused strongly alkaline ash, containing carbon and carbonic acid, from which was obtained,—

0.00170 grm. carbon.

0.29200 grm. chloride of silver.

0.00194 grm. phosphoric acid	} + carbon and carbonic acid, forming the portion of ash insoluble in water, calculated from the analysis of larger not weighed portions of the pancreatic secretion.
0.00086 grm. lime	
0.00036 grm. magnesia with traces of peroxide of iron	

0.430 grm. chloride of potassium + chloride of sodium, whence

0.140 grm. platinochloride of	{ 0.3872 chloride of sodium.
potassium; hence	{ 0.0428 chloride of potassium.

B. Physical properties as before.

83.107 grms. of the fresh secretion left 1.668 grm. of residue dried at 230° F.; this, heated to redness, gave 0.7477 grm. of ash containing carbon and carbonic acid; whence,—

0.0077 grm. carbon.

0.880 grm. chloride of silver.

0.00414 grm. phosphoric acid	} calculated as above.
0.0045 grm. lime	
0.0014 grm. magnesia with trace of peroxide of iron	

0.832 grm. chloride of potassium + chloride of sodium, whence

0.28800 grm. platinochloride of	{ 0.7311 chloride of sodium.
potassium; thus.	{ 0.0943 chloride of potassium.

C. Physical properties as before.

80.556 grms. of the fresh secretion left 1.267 grm. of residue dried at 230° F.; this, when heated to redness, gave 0.691 grm. of ash containing carbon and carbonic acid; whence,—

0.0105 grm. carbon.

0.544 grm. chloride of silver.

0.00219 grm. phosphoric acid	} calculated as above.
0.00225 grm. lime	
0.0007 grm. magnesia	

0.740 grm. of chloride of potassium + chloride of sodium, whence

0.199 grm. platinochloride of	{ 0.6792 chloride of sodium.
potassium; thus.	{ 0.0608 chloride of potassium.

Hence there exist in 1000 grms. of the pancreatic secretion,—

	I. Taken from a permanent fistula.				II. From a temporary fistula, immediately after the operation.	
	A.	B.	C.	Mean.	A.	B.
Water	976·780	979·930	984·630	980·45	900·76	884·4
Solids	23·220	20·070	15·370	19·55	99·24	115·6
Organic matter (ferment)	16·380	12·450	9·210	12·71	90·44	
Inorganic bases and salts	6·830	7·520	6·160	6·84	8·80	
Soda (combined with the ferment)	3·818	2·858	3·249	3·31	0·58	
Chloride of sodium	1·917	3·484	2·110	2·50	7·35	
Chloride of potassium	1·008	1·059	0·738	0·93	0·02	
Phosphate of lime	0·051	0·100	0·051	0·07	0·41	
Phosphate of magnesia, with traces of peroxide of iron ...	0·024	0·006	0·005	0·01	0·12	
Phosphate of soda (tribasic) ...	0·015	...	...	0·01		
Lime (combined with the ferment) ...	...	...	...	...	0·32	
Magnesia (combined with the ferment) ...	...	0·015	0·006	0·01		
	6·833	7·522	6·159	6·84	8·80	
Specific gravity	...	1·0106	...	...	1·0306	

In regard to the above results, the author maintains that the considerable differences evident in them cannot be attributed to the mere absorption of water, which might be occasioned by the operative procedure; nor to the evaporation of water during the collection of the secretion; but is in favour of the view, that they must be ascribed to a reaction of innervation, similar to that pointed out by Ludwig in the case of the salivary glands, and Bernard in that of the kidneys after irritation of the glandular ducts.

The author retains his former opinion upon the negative action of the pancreated fluid in the digestion of albuminous and fatty matters; but he alters it in regard to the relation of the pancreatic juice to the intermediate intestinal circulation; after the formation of permanent fistulæ in the same genus of animal (the dog), this stands with respect to the hepatic and gastric secretion as follows:—

The body of an animal (dog), weighing 1 kilogram., secretes in twenty-four hours,—

		Water.	Organic matter.	Inor- ganic matter.	Muriatic acid.	Soda.
Gastric juice containing saliva...	100 grms. containing	97·12	1·75	1·13	0·270	
Bile	20 grms. containing	19·01	0·99	0·10	...	0·059
Pancreatic juice	89 grms. containing	87·24	1·15	0·61	...	0·293
Total	209 grms. containing	203·37	3·89	1·84	0·270	0·352
					; = 0·229 NaO	

If the entire quantity of blood circulating be placed at 200 grms., viz. 176 grms. for the water, 22·41 grms. for the organic matter, and 1·59 grms. for the inorganic matters, the chlorides of sodium and potassium amounting to 0·89 grm., it is evident that half the water

and two-fifths of the inorganic salts are secreted into the intestine through the medium of the pancreas in twenty-four hours, and again taken up into the circulation; further, that more than half of the chloride of sodium is daily separated into muriatic acid and soda, the acid of which is again secreted by the gastric glands, and the base by the pancreas, so as, after having combined in the further course of the intestine, and forming chloride of sodium, to be again absorbed.

In the case of a man weighing 64 kilogrms., the author, judging from the experiments upon dogs, estimates the quantity secreted daily at 4.6 kilogrms. A man of the above weight expires daily on an average, within twenty-four hours, 786 grms. of carbon, and secretes 32 grms. of urea, equivalent to,—

92.70 grms. of albuminous matter =	42.73 grms. of carbon of respiration.
786 grms. of carbonic acid =	214.36 grms. of carbon.

Difference..... 171.63 grms. of carbon,

equivalent to 386.17 grms. of starch, requiring for its conversion into a form fit for respiration, 82.66 grms. of pancreatic juice.

Hence of the 4.6 kilogrms. of pancreatic juice secreted daily, 0.08 kilogr. is sufficient for the proper digestive functions. Now as purely carnivorous animals have comparatively larger salivary glands than herbivora of the same orders; moreover, as the digestion of fatty and albuminous matters takes place as readily when the pancreatic juice is absent as when it is present; the author concludes that the pancreatic secretion serves principally to produce the intermediate circulation of water; and after the muriatic acid has become separated from the chloride of sodium, to eliminate the feebly combined soda accumulated in the general mass of circulating blood, in the form of a strongly alkaline compound of soda and albuminous matter (diastase and soda), so as to restore the typical equilibrium between the acids and bases; hence it can only be regarded as an accessory agent in true digestion.—*Ann. der Chem. und Pharm.*, vol. xcii. p. 33-41.

On the Formation of Ammonia from Non-nitrogenous Substances and Nitric Acid. By A. OVERBECK.

The mother-liquor from the preparation of camphoric acid (camphor was heated with nitric acid) was evaporated on the open fire, when a black shining resin separated; this, when burnt on platinum foil, evolved a strong odour of burnt horn. On the addition of carbonate of soda, the fluid evolved an ammoniacal odour. Hence the author concludes that various organic substances will furnish ammonia by dry distillation after treatment with nitric acid.—*Archiv der Pharm.*, lxxx. p. 144.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Remarks on the Theoretical Views of the Constitution of Organic Substances. By HEINRICH WILL.

Now that the views respecting the constitution of organic substances are beginning to assume a more definite form, and the excessive accumulation of particular facts demands a careful arrangement according to a uniform system, it may not be considered inappropriate to attempt a thorough discussion of those points, upon which there may be a diversity of opinion as to the position of the molecules in an organic substance, and which may be characterized as determinative in the selection of a system.

Almost all chemists are unanimous in the opinion, that in organic substances two or more elements are intimately combined into groups which perform the functions of elements, being convertible from one state of combination to others, capable of replacing elements in combination, in definite equivalent proportions, and with definite relations of weight and volume. It is also quite agreed to designate these groups of elements by the general name of radicals; they may likewise be called compound elements.

It must be assumed of these radicals, that in replacing a simple element in any compound, they do so not only in definite proportions by weight, but also with definite relations of volume, that in the compound, they occupy the equivalent space of that element which is their type.

The radical cyanogen combines with hydrogen, volume for volume, without condensation, exactly in the same manner as the elements chlorine, bromine or iodine; and the cyanogen may be abstracted from the compound produced, in the same manner as any one of the simple elements from the corresponding compounds, hydrogen being left, equal in volume to one-half that of the compound; and it is therefore to be inferred that cyanogen occupies the same volume in the hydrogen compound as chlorine, &c. in the corresponding compounds. Equivalents of chloride, bromide, iodide, or cyanide of æthyle occupy in the state of vapour exactly the same volume as an equivalent of the hydrogen compounds of these haloids; and it is therefore to be inferred that the volume occupied by the alcohol radical in these volatile compounds is the same as that occupied by hydrogen, the type of the alcohol radical, in the hydrogen acids.

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Equivalents of formic acid, and its congeners of the general formula $C^{2n}H^{2n}O^4$, occupy in vapour equal volumes; the higher member of the series differs from the one immediately preceding, in the replacement of a part of the hydrogen of the initial member of the series by a higher alcohol radical. Since the vapour volume of the substance does not change with the equivalent in the substitution of higher radicals, we are justified in concluding that these radicals occupy exactly the same space in the individual substances as the hydrogen which they replace. The same view applies to homologous series of hydrocarbons, alcohols, aldehydes, acetones, as well as to the homologous volatile bases; its applicability to æthers and anhydrides is as yet undecided.

The same relation of volume obtains in substitution derivatives as in the original substances. Benzole, $C^{12}H^6$, occupies in vapour the same volume as equivalents of nitrobenzole, $\left. \begin{matrix} C^{12}H^5 \\ NO^4 \end{matrix} \right\}$; acetic and chloracetic acids present an equal condensation of their constituent elements; and whatever may be assumed as to the relative position of the atoms in these two acids, the facts that the essential chemical or physical characters of the original substance are not altered, and that the chlorine may be replaced by hydrogen with reproduction of acetic acid, prove that chlorine, and the hydrogen replaceable by it, occupy equal space and similar position in the two substances. The theory of substitution in this sense is no longer questioned; it is only with regard to the original position or arrangement of the molecules that a diversity of opinion prevails.

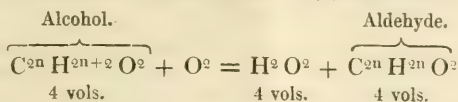
The formulæ for organic substances, which may be considered as most fully investigated, and with regard to whose equivalents there is no longer any doubt, show that there are scarcely any which contain an uneven number of carbon atoms ($C=6$ or $O=8$); every modern investigation of substances, to which formulæ with uneven numbers of carbon atoms have been assigned, *e. g.* salicine, quinone, harmaline, coniine, thebaine, narceine, &c., has the result of changing these formulæ to others with even numbers of carbon atoms.

Without any reference to the cause of this general fact, it must be recognized as the expression of a uniformity, as an empirical law, the direct and most simple statement of which is, that in the formation or decomposition of organic substances, even numbers of carbon atoms are always brought into play. The prevalence of this uniformity is now so universally admitted, that any further demonstration would be superfluous. It is known that the exceptions to this uniformity that might be urged in the case of gallic, croconic, citraconic acids, &c., have been shown to be only apparent, and a consequence of the polybasic character of these substances.

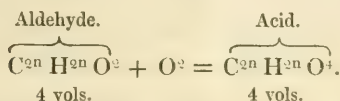
Another uniformity of a similar kind is the fact, that when organic substances lose or assimilate oxygen or sulphur, for instance in the form of their hydrogen compounds, these latter come into play with an acting value which is not expressible by the equivalent generally adopted ($HO=9$, $HS=17$), but by double this equivalent ($H^2O^2=18$, $H^2S^2=34$), or by a multiple of this latter.

Since the prevalence of this uniformity is less generally admitted, and since the families of organic substances for which it is considered that this uniformity does not obtain, are precisely those whose constitution is undecided, it may be well to bring forward some evidence in support of it.

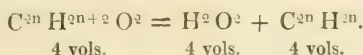
All alcohols, in their conversion into aldehydes, assimilate 2 molecules of oxygen ($O=8$); the water separated has the acting value $H^2 O^2=18$. So likewise aldehydes, in their conversion into an acid (monobasic), assimilate 2 molecules of oxygen; thus,—



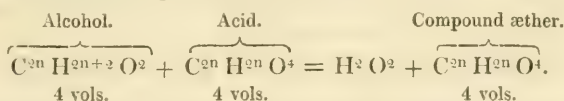
and



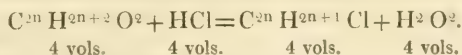
All alcohols are convertible, by abstraction of their oxygen, into hydrocarbons, $C^{2n} H^{2n}$, which have an equivalent volume equal to the water separated:—



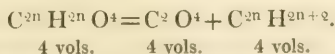
In the conversion of alcohols into compound æthers by a monobasic acid, $H^2 O^2$ is separated,—



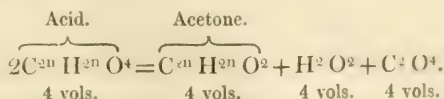
Again, in the conversion of alcohols into chlorine, bromine, or iodine compounds of the radicals, the same relation obtains:—



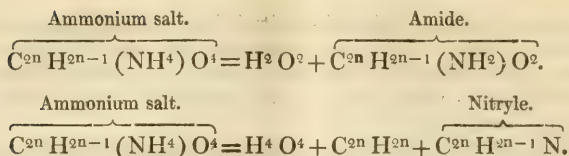
All the monobasic organic acids are broken up, when heated with excess of alkaline base, into carbonic acid and hydrocarbons:—



The same acids yield acetones, water, and carbonic acid when their neutral salts are heated:—



The amide of a monobasic acid differs from the neutral ammonium-salt of the same acid by containing $H^2 O^2$ less; the nitrile differs by containing $H^2 O^4$ less:—

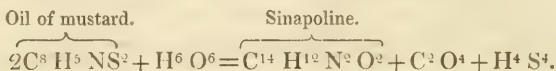


A polybasic organic acid always loses under the influence of heat $\text{C}^2 \text{O}^4$, or $\text{C}^4 \text{O}^8$, or $\text{H}^2 \text{O}^2$, $\text{H}^4 \text{O}^4$, $\text{H}^6 \text{O}^6$. The same uniformity in the acting value of the eliminated water obtains in the conversion of a polybasic acid into an æther acid, or a neutral æther into an amine acid, an amide, or an imide; likewise in the partition of sugar and other fermentable substances under the influence of yeast. In the formation of a fat from an acid and the polybasic alcohol glycerine, the water eliminated always amounts to 2, 4, or 6 equivs. It seems evident that this relation, if admitted to be uniform, is owing to the existence of even numbers only of oxygen atoms ($\text{O}=8$) in organic substances.

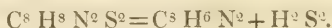
The same holds good for sulphur, selenium and tellurium; no organic substance, whose equivalent is known with certainty, contains an uneven number of sulphur atoms.

The substances corresponding to alcohols, aldehydes, and monobasic acids contain 2 atoms of sulphur in the place of 2 atoms of oxygen; the sulphur molecule ($\text{S}^2=32$) is equally indivisible with the oxygen molecule ($\text{O}=16$).

Mustard-oil breaks up, in contact with water and a metallic oxide, into sinapoline, carbonic acid and sulphuretted hydrogen:—



Thiosinamine breaks up into sinamine and sulphuretted hydrogen:—



It is certainly not a mere accident, that in the latter instance, where only sulphur and hydrogen are eliminated, the equivalent of the substance remains the same in respect of the amount of carbon, while in the former instance, where sulphur and carbon are eliminated in the proportion $\text{C}^2:\text{S}^4$, the equivalent of the substance is augmented to C^{14} . In the same manner, the production of acetone, $\text{C}^{2n} \text{H}^{2n} \text{O}^2$, from 2 atoms of an acid, $\text{C}^{2n} \text{H}^{2n} \text{O}^4$, must be regarded as a consequence of the indivisibility of the carbon and oxygen molecules.

A close and impartial consideration of the formulæ assigned to organic substances, as the result more particularly of recent investigation, will at once show that the number of instances in which this uniformity was not perceived has gradually become less; and no chemist can fail to perceive that the adherence to this uniformity, first recognized by Gerhardt and Laurent, has, in the hands of those chemists and of Strecker, been an instrument of great service, by

the aid of which the possibility was afforded of classifying organic substances in a systematical manner.

As the existence of this uniformity in the weight of the carbon, oxygen, or sulphur particles which take part in the formation or decomposition of organic substances, is but little doubted, the theoretical consequences which follow from it, and have a direct relation to the volume of the existing substance or its derivatives, must likewise be admitted.

The seat of the formation of organic substances is the plant-cell; in it there are produced from three universally diffused substances, water, carbonic acid and ammonia, the unnumbered variety of substances presented by the plant. In the hands of the chemist the number of known substances has been increased hundredfold, and the possibility of their further multiplication appears indefinite.

The uniformity already pointed out in the weights of the carbon and oxygen molecules in organic substances renders it, as it were, a condition of their formation, that a quantity of water and of carbonic acid should be brought into play corresponding at least with the formula $C^2O^4=44$ or $H^2O^2=18$. It is indifferent whether it is assumed that these quantities are simple equivalents or that they are double equivalents; the fact is obvious, that the spaces occupied by equivalent quantities of both substances in the state of vapour are equal, and, with the acting value by weight with which they contribute to the formation of organic substances, they are likewise equal to the space occupied by an equivalent of ammonia. Assuming that the equivalent of carbonic acid is $44=C^2O^2$, that of water $18=H^2O^2$, and that of ammonia $7=NH^3$,—equivalents of these three substances, from which all organic substances are produced, have volumes that are equal, and four times as great as that of an equivalent of oxygen ($O=8$), twice as great as an equivalent of hydrogen ($H=1$), or an indivisible oxygen molecule ($O=18$). For the two oxygen compounds, water and carbonic acid, the condensation of the elements is as 6 : 4 (or as 3 : 2); for ammonia it is as 8 : 4 (or as 4 : 2). In the latter instance it may be assumed that the condensation is equal for both elements, nitrogen and hydrogen, equivalents of which occupy equal volumes. In the combination of 4 vols. of hydrogen (2 equivs.) and 2 vols. of oxygen (an indivisible molecule), it is probable that the condensation is confined solely to the hydrogen, and that it is the same as in the formation of ammonia, amounting to one-half its volume. Since the atomic theory admits only a juxtaposition of the smallest particles, and since the relative position can never be ascertained by observation, it is certainly allowable to represent the arrangement of these smallest particles with reference to the relations of volume of these three substances, which are so intimately connected with the genesis of organic substances, that they may perhaps be regarded as their most simple types; and this is more particularly the case, since the usual chemical formulæ are merely representations of the arrangement of the smallest particles with reference only to the relations of weight. The following mode of expression may be adopted for water, ammonia and carbonic acid,

and it at least possesses the value of admitting, in its application to organic chemistry, of an explanation of the phænomena of production and decomposition of organic substances in accordance with the radical theory, both in the relations of volume and weight:—

Water.		Ammonia.		Carbonic acid.	
H	O ²	H	N	C ² O ²	O ²
H		H	H		
6	:	4	8	:	4
Condensation.					

The fact, that the original materials for the production of organic substances occupy in the gaseous state equal volumes—that their elementary atoms, which, both in relation of volume and weight, have unequal acting values, are by their juxtaposition reduced to equal volumes—is of great significance from the point of view afforded by the radical theory; and its importance is increased by the circumstance, that equivalent quantities of all volatile organic substances—whether simple or complex in their elementary composition, whether of large or small atomic weight, whether acid, neutral or basic—possess in the gaseous state the same volumes as equivalent quantities of water, ammonia or carbonic acid. It is evident that this uniformity in the function by volume of substances containing compound elements, is most intimately connected with the uniformity in the function of the three substances which have been characterized as the sources from which they are produced, and which contain simple elements. Either the uniformity in volume determines the uniformity with regard to weight, or the reverse; it is evident that if the atomic weight of oxygen is taken as 8, the equivalent of an organic substance cannot contain less than 2 atoms of carbon or of oxygen.

The volatile organic substances for which this uniformity in the relations of volume and weight do not obtain, when the formulæ that have hitherto been employed to express their equivalents are retained, are the æthers, $C^{2n}H^{2n+1}O$, and some analogous substances; the equivalents of the anhydrous acids discovered by Gerhardt are likewise disputed.

In determining the equivalents, as well as the rational formulæ for organic substances, the physical characters are of as much importance as the chemical; and sometimes the former are more serviceable, for it is known that there is a definite connexion between the physical, as well as the chemical characters on the one hand, and the kind and quantity of the constituent elements, as well as the mode in which they are arranged in equivalent volumes on the other.

All the members of such families of organic substances in which

the arrangement of elements is simple, which contain as it were only a single group of atoms consisting of simple or compound elements, are volatile without decomposition; their elements are held together by chemical affinity as a complete whole, even under the influence of heat. Substances which contain several such groups of atoms are, generally speaking, not volatile. Other substances, again, exist which are either decomposed by heat, or without decomposition assume different physical characters, and these form the transition. The physical characters of organic substances are intermediate between those of their constituent elements—on the one side carbon, on the other hydrogen, nitrogen and oxygen. No organic substance is known which retains permanently the physical state of any one of the latter elements, and is not reducible, by pressure or abstraction of heat, to a liquid or solid state; nor are there any which present the physical characters of carbon, and cannot, by the influence of heat, be rendered, at least partially, liquid or gaseous. The point at which, without decomposition, the physical condition of an organic substance changes under the influence of heat, is dependent, on the one hand, upon the number and relation of the elementary atoms comprised in a certain equivalent volume, and, on the other hand, upon their relative position. It is known that the melting-point, as well as the boiling-point, bears a definite relation to the constitution, a relation which, since the investigations of Kopp, must be regarded as constant as the relations of weight and volume which obtain in combination. If this relation between the boiling-point and constitution appears in some instances contradictory or obscure, its actual existence must not on that account be questioned, or its importance denied in other instances where the accuracy of the observations is not doubtful. The uniformities of the relations of weight and volume in combination, were inferred only from a series of careful observations; and now that there is such preponderating evidence for their generality, the few facts which may be interpreted in a contrary sense can no longer furnish a reason for doubting the validity of the law of multiple proportions. The recognition and demonstration of a uniformity is not alone dependent on the accuracy of observations, but likewise upon their number.

It is now known with certainty that there are uniformities in the difference between the boiling-points of organic substances, which there is reason to assume have a like arrangement of simple and elementary elements. There is as little possibility of doubting the approximative accuracy of the boiling-points of ordinary æther and alcohol, for instance, as of doubting the reality of a connexion between these boiling-points and the constitution of the substances.

The boiling-point of æther is frequently brought forward in argument for the opinion that the formulæ of that substance should be C^4H^6O , and not $C^4H^{10}O^2$, because if it is a rule that substances of higher atomic weight have a higher boiling-point, this æther should boil at $211.9^\circ F.$ (as $C^4H^6O^2$ differs from $C^4H^{10}O^2$ by $2C^2H^2$), while it really boils at $95.9^\circ F.$ It would be hardly possible to find any objection less tenable and more easy to remove

than this; indeed there is scarcely any character of æther that furnishes more decided evidence for the duplication of its formula than the boiling-point. The law of uniform increment in the boiling-points obtains only for such homologous series of substances in which the radical producing the difference of $C^2 H^2$ alters the acting value of the original radical in the relation of weight, but not in that of volume; and in this sense alcohol and æther are not homologous. The volumes of equivalent weights of the several members of the alcohol series or the monobasic acids, &c., are equal, but the boiling-points differ. The boiling-point is a specific character, the vapour-density (identity of equivalent volume) is a generic character; the variation of the former is dependent upon that of the latter. It is probable that the reason why alcohol and æther boil at a lower temperature than water will never be ascertained; but if the existence of a uniformity, of a law derived from the comparison of a series of trustworthy observations can at all serve for the explanation of a phænomenon, the proximate cause of the lower boiling-points of alcohol and æther may be given.

By assuming, as the starting-point in a comparison of water with the alcohols, æthers, acids, &c., that the equivalent of the former is not that usually taken, but the weight which in vapour has the same volume as an equivalent of any one of the substances in question, it will then be represented by the formula $H^2 O^2$. Alcohol may be regarded as $C^4 H^5 O$, HO , or as $\left. \begin{smallmatrix} C^4 H^5 \\ H \end{smallmatrix} \right\} O^2$; it is in both cases evident that an equivalent of æthyle is substituted in the place of an equivalent of hydrogen. Let us compare the boiling-point of water and those of the alcohols:—

	Formulae.	Boiling-points.	Differences.
Water	$H^2 O^2$	212° F.	
Methylalcohol . . .	$\left. \begin{smallmatrix} C^2 H^3 \\ H \end{smallmatrix} \right\} O^2$	140°	— 72°
Æthylalcohol	$\left. \begin{smallmatrix} C^4 H^5 \\ H \end{smallmatrix} \right\} O^2$	173°·3	— 38°·7
Propylalcohol	$\left. \begin{smallmatrix} C^6 H^7 \\ H \end{smallmatrix} \right\} O^2$	205°·7	— 6°·3
Butylalcohol	$\left. \begin{smallmatrix} C^8 H^9 \\ H \end{smallmatrix} \right\} O^2$	233°·6	+ 21°·6
Amylalcohol	$\left. \begin{smallmatrix} C^{10} H^{11} \\ H \end{smallmatrix} \right\} O^2$	269°·6	+ 57°·6

We see that an equivalent of methyle ($C^2 H^3$), which is substituted for 1 equiv. of hydrogen without altering the volume-equivalent, reduces the boiling-point of water 72 degrees. Each further atom of methyle, which replaces hydrogen in the radical itself (inasmuch as æthyle, $C^4 H^5$, must be regarded as methyle in which an equivalent of hydrogen is replaced by methyle, $\left. \begin{smallmatrix} C^2 H^3 \\ C^2 H^3 \end{smallmatrix} \right\}$, &c.), raises the boiling-

point of the succeeding member about 36° . Consequently the substitution of hydrogen by æthyle reduces the boiling-point about 36° or 38° .

[To be continued.]

On a new Organic Acid containing Phosphorus.

By J. FRITZSCHE.

Several years ago the author made experiments with the view of preventing as far as possible the separation of pure alcohol from the mixture of oil of turpentine and spirit employed in lighting streets. As an addition for this purpose, he selected a solution of phosphorus in coal-naphtha. In a solution of this description which had been kept a considerable time, he observed the formation of a phosphuretted body, which forms the subject of this paper.

Preliminary experiments showed, that for the production of this new body, the solution of phosphorus must be exposed to a considerable extent to the atmospheric oxygen, and that the quantity of water dissolved in the coal-naphtha did not prevent its formation, although a larger amount of water delays it. The new body is best obtained in the following manner:—1 part of well-dried phosphorus is dissolved with the assistance of heat in from 90 to 100 parts of coal-naphtha, containing as little water as possible; the solution, when tolerably cool, is poured into shallow glass vessels, which are covered with glass plates, and left standing quietly, until the deposit, which is at first voluminous and flocculent, has attracted moisture and contracted into a transparent, yellow, semifluid mass. Treated in this manner, 2 drms. of phosphorus, which were dissolved in 24 oz. of coal-naphtha, furnished 11 drms. of the semifluid product.

The contraction of the flocculent mass may be facilitated by pouring away the fluid as soon as it has become clear above the deposit, or still more by the addition of a few drops of water and strong stirring, by which means the separation of the acid in the form of a syrupous mass, is effected in a few moments, even in fluids which have become completely gelatinous.

The phosphoric solution is first of all poured away from the crude product, which is washed with coal-naphtha. If water be poured over the semifluid mass thus obtained, and the whole be stirred up, a sort of emulsion is formed, a portion being dissolved, whilst the remainder is only mechanically suspended. The watery solution will be more or less milky in proportion to the amount of coal-naphtha adhering to the mass. The filtered solution is still milky, but usually becomes perfectly clear after standing for some time, from the deposition of drops of a tougher consistence. When heated, the milky solution diffuses a strong leek-like odour; and even when it has become clear, it is usually rendered turbid by evaporation: drops of a tougher consistence then gradually separate, but these dissolve again at length when the concentration is carried further, and the residue forms a homogeneous syrupous fluid. This now no longer possesses an alliaceous odour, but is peculiarly aromatic, and

when diluted with water usually remains clear to a certain extent, but becomes opalescent again with a larger quantity of water.

The milky solution has an acid reaction and taste; it contains phosphoric acid, sometimes only in traces, but occasionally in large quantities, as may be proved by the formation of a crystalline precipitate on supersaturation with ammonia and the addition of a solution of magnesia.

If the mass be treated for a second time with water, the latter dissolves a portion of it, and then exhibits the reactions of the new acid. This however constitutes the great bulk of the insoluble residue, which forms an opaque, more or less intensely yellow, turpentine-like mass, specifically heavier than water, and but sparingly soluble in that fluid. It dissolves readily in alcohol, but still usually leaves a small quantity of a yellow substance undissolved; this greatly resembles freshly-precipitated sulphuret of arsenic in appearance, and when washed with alcohol and dried, either retains its pulverulent consistence and citron-yellow colour, or cakes together into hard orange-coloured fragments. This yellow body is insoluble in alcohol, but when it is covered with the alcoholic solution of the acid and exposed to the action of the sunlight, it disappears in a short time. It contains much phosphorus.

Towards alkalis the yellow body behaves to a certain extent like an acid, for when the yellow semifluid mass is treated with watery alkaline solutions (both of caustic alkalis and alkaline bicarbonates), the yellow body is also dissolved. If only a small quantity of water be employed, and the solution be mixed first with alcohol and afterwards with muriatic acid, the resinous acid remains in solution, but the yellow body separates in flakes. If these be collected on a filter, and treated, whilst still moist, with a solution of bicarbonate of soda, they are again dissolved, and may be again precipitated by acids; they behave in the same way with caustic ammonia, and partly also with caustic potash; but in general the behaviour of this yellow body was not always the same, and it varies especially according as it is freshly precipitated or dried. In the dry state it was scarcely soluble in alkalis, but changed its colour instantaneously to a dirty brown; the yellow colour is reproduced by acids. In a solution of caustic potash, an evolution of gas commenced even at ordinary temperatures; this became more considerable on the application of heat, and had a strong alliaceous odour.

From what has been stated, the new acid is contained in the alcoholic solution, in which however free phosphoric acid also occurred. To obtain the new acid as pure as possible, the crude product of oxidation is extracted with water, the residue is dissolved in strong alcohol, and filtered for the removal of the yellow insoluble body. Ammoniacal gas is passed into the clear alcoholic solution until it has acquired a strong ammoniacal odour, when it is left standing for twenty-four hours, and decanted and filtered to separate the fluid portion from solid deposits; the former is then distilled to get rid of the alcohol. The residue is dissolved in water, with the addition of ammonia if necessary, and muriatic acid is added to the clear solu-

tion as long as this produces a milky turbidity; the consolidation of the resinous acid which separates is facilitated by stirring the fluid strongly; the latter is afterwards poured away, and got rid of as completely as possible by washing the acid, which adheres to the walls of the vessel, with water. The acid is dissolved in as little alcohol as possible, and thrown down from this solution by means of water, when it separates in the form of a brownish, opaque, turpentine-like mass. This is separated as far as possible from the watery fluid, and heated afterwards in the water-bath, when it gradually becomes clear from the evaporation of the mechanically-intermixed water, and at last forms a transparent brownish resin, which is thickly fluid at the temperature of boiling water, but at ordinary temperatures presents a tough sticky consistence.

The acid thus prepared expels carbonic acid from carbonates. The salts of the new acid were not found to possess a constant composition. The cadmium-salt however gave on analysis,—

	I.	II.	III.
Carbon	32·30	33·72	38·05
Hydrogen	4·95	5·14	5·78

These numbers at least agree so far, that the relation between the carbon and hydrogen is nearly the same in all. In II. and III. the author found 15 per cent. of phosphorus. It is evident that the carbon and hydrogen are not contained in the substance in the same proportions as in coal-naphtha.

The alkaline salts of the new acid are very soluble, and dry on evaporation into gum-like masses. Their solutions furnish flocculent precipitates with earthy and metallic salts; these are insoluble in water, or at least dissolve in it with great difficulty. Perchloride of mercury is not precipitated at ordinary temperatures; but when heated, or even left standing for a long time without heat, a precipitate is formed. Nitrate of silver is precipitated in white flakes at the ordinary temperature; these however soon acquire a brown colour by standing in the air, and when heated with the fluid become dark reddish-brown. The texture and colour of the precipitates obtained in this last reaction vary considerably, according to the strength of the solutions employed and the length of time the whole is boiled; the precipitate is sometimes a heavy powder, which exhibits a golden-green lustre on the filter, and cakes together on drying into solid fragments, which present the same colour on their glassy fractured surfaces.

The new acid exhibits a peculiar behaviour towards chromic acid. If a solution of one of its alkaline salts be mixed with a solution of bichromate of potash, no precipitate is produced at first; but if the mixture be left quiet, a pulverulent body, of a pale green colour, is deposited by degrees. This separation takes place very soon when the fluid is heated to boiling and kept at that temperature for some time, especially if a little free acid be added to it. During the boiling a peculiar odour is evolved, and an abundant precipitate separates; this is of a more or less green colour, and usually dissolves

completely in ammonia to form a dark green fluid. From this solution acids precipitate a gelatinous body, usually of a less decided green colour than the product employed for the solution; the latter still remains green. The gelatinous body contracts on drying into hard fragments, if the solution was precipitated in the cold; a pulverulent product is also sometimes obtained when the precipitation is effected at a boiling heat. On evaporation, the ammoniacal solution dries to a deep green varnish-like mass, which exhibits no traces of crystallization, and no longer dissolves completely in water; it swells in that fluid, and gives up to it a small quantity of a yellow substance. Preliminary analytical experiments gave in one instance 46 per cent C. and 33 per cent. of residue on heating to redness; in another case, 32 per cent. C. and 60 per cent. residue.—*Bull. de St. Pétersb. Cl. Phys. Math.*, xiii. p. 177.

Notes on a Microchemical Reaction of Cholesterine and the Amyloid Corpuscles. By J. MOLESCHOTT.

M. H. Meckel's discovery, that cholesterine, treated with concentrated sulphuric acid and iodine, acquires, amongst other colours, a blue tint resembling that of cellulose, has reminded me of a result at which I arrived several years ago, namely, that a carmine, violet, or lilac colour may be given to cholesterine by means of sulphuric acid, without the addition of any other agent than pure water.

When cholesterine is treated with a mixture of 5 vols. of sulphuric acid and 1 vol. of water, and the crystals are exposed for a few seconds to a very gentle heat, microscopic examination shows that their edges have acquired a very bright carmine colour. With a mixture of 3 vols. of acid and 1 of water, the edges of the rhomboidal tablets acquire a violet colour, if the preparation be gently heated after being covered with a thin glass plate. A still more dilute acid gives the crystals, of which the edges flow into little drops, a lilac colour. A mixture of 14 vols. of acid and 1 vol. of water produces a reddish-brown colour, beside which carmine is also observable, especially in the midst of large aggregations of the rhomboidal tables. With from 5 to 14 vols. of acid to 1 vol. of water, the reddish-brown colour is more or less mingled with carmine, which does not appear when cholesterine is treated with concentrated sulphuric acid, which destroys the crystals.

From these observations it appears that the following colours may be produced at pleasure, by treating cholesterine with more or less concentrated sulphuric acid, and exposing the mixture more or less to the air,—reddish-brown, carmine, violet and lilac. The most diluted acid and the most complete action of the air give the lilac colour, whilst the mixture of 14 vols. of acid with 1 vol. of water produces the reddish-brown and carmine, which change more or less to violet if the preparations be kept for two hours exposed to the air. By keeping a longer time, the crystals treated with diluted mixtures are decolorized.

As to the amyloid corpuscles, which M. Virchow believes to be

composed of cellulose, whilst M. Donders regards them as starch, I imagine that they consist of cellulose which has become partially converted into starch. Thus these corpuscles acquire a blue colour by the action of iodine alone, and the colour becomes deeper on the addition of sulphuric acid (2.2 vols. of acid to 1 of water). In the former property they agree with starch, in the latter with cellulose. — *Comptes Rendus*, Feb. 12, 1855, p. 361.

On the preparation of pure Carbonate of Potash. By M. BLOCH.

With the view of avoiding the trouble of purifying the cream of tartar and the destruction of an equivalent of tartaric acid in the preparation of pure carbonate of potash, the author has employed the following method.

The bitartrate of potash is boiled with its equivalent of carbonate of lime. The liquid is filtered, and a few drops of nitric acid are added to it; the contained chloride is then precipitated by a few drops of nitrate of silver. The liquid is then passed through a filter moistened with water acidulated with pure nitric acid, evaporated to dryness in an iron pot, and the residue exposed to a red heat. A little water is sprinkled on the red-hot mass, in order to decompose the cyanide which has been formed. It is advisable to keep the materials constantly stirred, in order to equalize the reactions and obtain a homogeneous mass. The whole is then treated with pure water, filtered, and evaporated to dryness.

The carbonate thus prepared is perfectly pure, and contains no trace of chloride, a body which it was exceedingly difficult to get rid of by the old methods. The other advantage attending it is, that an equivalent of tartaric acid is obtained from every equivalent of bitartrate of potash employed, being thrown down in the first instance in the form of insoluble tartrate of lime. — *Comptes Rendus*, Feb. 12, 1855, p. 364.

Note on two Homologous Glucosides. By W. MAYER.

In a previous memoir* I have given my investigation of the resin of the rhizomes of *Convolvulus Schiedeanus*, Zucc., the jalap-resin of the so-called tuberoso roots. In continuation of this, the resin of *Ipomœa orizabensis*, Pell., the jalap-resin of the so-called stalky roots, was submitted to careful examination, as it appeared probable that this resin might consist essentially of a glucoside. This supposition has been confirmed. It appears further that the two resins are homologous, and distinguished from one another by $3(C^2H^2)$. The conjuncts of the sugar in the two resins consequently also differ by $3(C^2H^2)$, and the splitting by various reagents takes place according to the same definite proportions.

The glucosides, which are insoluble in water, are converted into soluble bodies by treatment with aqueous solutions of alkalis or alkaline earths; these soluble bodies have a very strong acid reaction, and form compounds with bases. These glucoside acids differ from

* Chem. Gaz., vol. xi. p. 21.

the *glucosides* only by several atoms of water, which are introduced into the latter. The determination of the atomic weight from the compounds of the glucoside acids with bases, cannot afford decisive results, their affinity for bases being, like that of the tannic acids, not very great. It appears very probable that they form three series of salts with 1, 2, and 3 eqivs. of base; they are tribasic, as Strecker has recently shown to be the case with the tannic acid of nut-galls. Compounds of salts of one series with those of another are also formed very easily. These properties render the preparation of the salts very difficult, and produce an uncertainty in the determination of the atomic weight, which can only be got rid of by the study of the products of partition and decomposition.

The glucosides and glucoside acids furnish the same products of partition and decomposition. [Splitting by mineral acids (acetic and oxalic acids do not produce this effect) is accompanied by an assimilation of water. The conjuncts separated from the sugar have the formula $C^n H^{n-1} O^7$. They combine directly with alkalies and alkaline earths, undergoing at the same time a peculiar change. Thus, when again separated from their combinations with bases, they contain an atom less water, and have the formula $C^n H^{n-2} O^6$ or $C^n H^{n-3} O^5$. The neutral crystallized baryta compounds, dried at $212^\circ F.$, are expressed by the formula $C^n H^{n-3} O^5 + BaO$. In many of their properties these acids have a remarkably close similarity with those of the great series of fatty acids, upon which I shall return hereafter. They are crystallizable from alcohol and æther, have an acid reaction, and form salts, which were partially obtained in a crystalline form.

The glucosides are also split by fusing alkalies, furnishing the acids $C^n H^{n-2} O^6$ and oxalic acid, with evolution of hydrogen.

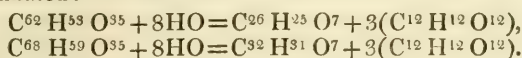
Emulsine likewise effects the resolution of the glucoside acids; but this experiment cannot be made with the glucosides, as these are insoluble in water. I cannot yet determine whether the bodies of the formula $C^n H^{n-1} O^7$ are obtained in this case, as I have hitherto only examined the baryta compounds.

The action of nitric acid upon the glucosides and glucoside acids, as well as upon the conjuncts, is very violent. In all these cases it produced ipomæic acid, $C^{10} H^9 O^4$, and oxalic acid.

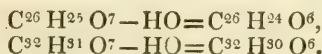
In consequence of this investigation, the formula which I proposed for the resin of *Convolvulus Schiedeanus* (rhodeoretine) must be altered. The compounds of rhodeoretic acid with bases furnished, as above stated, uncertain grounds for the determination of the atomic weight. This must be settled principally by the products of partition. In my previous memoir I have adopted a false atomic weight for the conjunct of the sugar in rhodeoretine, rhodeoretinolic acid, partly because I laid too much stress upon simple proportions in the salts of rhodeoretic acid, and partly because I took a crystallized baryta salt for the neutral salt, instead of an acid salt, which it now appears to be. The analytical results of my previous investigations agree as well or better with the new formulæ than with the old ones. I will shortly publish the particulars of my experi-

ments, so as to show my reasons for regarding my previous formulæ as incorrect.

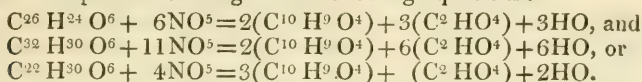
The resin of *Convolvulus Schiedeanus* received the name of rhodeoretine from Kayser, on account of the wine-red colour which is communicated to it by concentrated sulphuric acid. I retained this name, but regard it as unsuitable now, as the resin of *Ipomæa orizabensis* exhibits the same reaction. I consequently prefer the name of *convolvuline* for the former resin, and that of *jalapine* for the latter. The glucoside acids would then be convolvulic and jalapic acids; the conjuncts of the sugar in the glucoside acids, as they are obtained by mineral acids, will be convolvulinole and jalapinole, and after the loss of an atom of water by treatment with base, convolvulinolic and jalapinolic acids. Convolvuline has the formula $C^{62} H^{50} O^{32}$, jalapine $C^{68} H^{56} O^{32}$. Their conversion into the glucoside acids takes place by the reception of 3 atoms of water; the acids have the formulæ $C^{62} H^{53} O^{35}$ and $C^{68} H^{59} O^{35}$. In the cleavage of the glucoside acids by mineral acids, 8 atoms of water are assimilated:—



By the action of bases, convolvulinole and jalapinole lose 1 atom of water, and become converted into convolvulinolic and jalapinolic acids,—



The oxidation of convolvulinolic and jalapinolic acids by nitric acid takes place according to the following equations:—



The quantity of oxalic acid formed appears to be in favour of the first of the two equations for the decomposition of jalapinolic acid. This is also supported by the fact, that ipomæic acid is very probably bibasic, and perhaps belongs to the same series as succinic and suberic acids, &c.—Liebig's *Annalen*, xcii. p. 125.

On the Active Principle of Centaurea calcitrapa. By L. COLIGNON.

Centaurea calcitrapa exhibits a powerful febrifuge action. The author has endeavoured to prepare its active principle. This however is not an alkaloid, and cannot be obtained in a crystalline form. It has an intense and styptic bitter taste, has a transparent amber colour, and a syrupy consistence; it is not volatile, is decomposable by heat, strongly reddens litmus-paper, dissolves readily in alcohol and æther, but is only sparingly soluble even in boiling water; with potash, soda, and ammonia it forms soluble but uncrystallizable salts, and with lime and oxide of lead insoluble salts.

This substance, for which the author proposes the name of *calci-*

tragic acid, is obtained in the following manner :—The coarse powder of the entire plant, collected during the time of flowering, is exhausted with alcohol in a displacement apparatus, and the fluid thus obtained is agitated with a sufficient quantity of purified animal charcoal to remove the green colour. The fluid is then filtered, and eight-tenths of the alcohol distilled from it. On cooling, oily drops are formed on the surface of the fluid. It is then evaporated on the vapour-bath, when new drops are formed; these are gradually collected, and finally dissolved in æther. By the evaporation of the ætherial solution, the substance is obtained with the properties already described.—*Archiv der Pharm.*, 2nd series, lxxx. p. 186.

On the Periodides of the Compound Ammonias.

By M. WELTZIEN.

When ammonia is allowed to act upon iodide of æthyle, it appears that all the four ammonias of æthyle are formed. By exposure to the air, however, the iodide of tetraethylammonium is converted into periodide at the expense of the iodide of ammonium present.

Triiodide of Tetraethylammonium, $\text{NC}^{16}\text{H}^{20}\text{I}^3$.—This body is obtained in the form of acicular crystals, when the fluid procured by the action of alcoholic ammonia upon iodide of æthyle is heated with iodine. The author obtained crystals of considerable size from a solution which had been kept standing for months.

It is difficult of solution in cold water, but dissolves readily in boiling alcohol; the large crystals are obtained particularly from solutions of the salt in iodide of ammonium, iodide of potassium, and the conjugate ammonias. The large crystals obtained by the author were bluish-black, dark reddish-brown, transparent; splinters magnified 90 diameters varied from pale yellow to dark reddish-brown.

When boiled with an aqueous or alcoholic solution of potash, the compound was decomposed into iodide of potassium, iodate of potash, triethylamine and iodoform. A platinum salt was obtained by removing the iodine by the addition of an alcoholic solution of nitrate of silver to a similar solution of the iodine compound, and then getting rid of the excess of silver by means of muriatic acid. The solution was then evaporated, and chloride of platinum added to it, when tolerably large crystals of the regular system were obtained; these, as shown by analysis II., are tetraethylammoniochloride of platinum, $\text{C}^{16}\text{H}^{20}\text{NPtCl}^3$. Analysis I. is that of the triiodide of tetraethylammonium :—

I.					II.			
N	..	..	1	= 2.74	N	..	1	
C	18.30	17.75	16	18.79	C	28.70	16	28.62
H	4.58	4.50	20	3.91	H	6.60	20	5.96
I	74.88	74.93	3	74.56	Pt	29.20	1	29.51

The addition of water to the mother-liquor of the triiodide of tetraethylammonium separated a heavy, oleaginous, brownish-red

fluid, which has not yet been analysed, but appears to contain a still higher iodide of tetræthylammonium.

The fluid from which the substance just described separated furnished on dilution a saline mass, which was distilled with lime, so as to obtain the bases which it contained. The distillate was saturated with muriatic acid, and the nature of the bases determined by repeated crystallization after addition of chloride of platinum. Ammonio-chloride of platinum crystallized first; then æthylammonio-chloride, biæthylammonio-chloride and triæthylammonio-chloride of platinum.

Methyle Compounds.—If an alcoholic solution of iodine be added to a heated solution of iodide of tetramethylammonium, an abundant crop of metallic acicular crystals is obtained; these are the—

Pentiodide of Tetramethylammonium, $C^8 H^{12} NI^5$, which is decomposed by boiling with water, forming on the one hand iodide of tetramethylammonium, and on the other iodides of the same base with still larger amounts of iodine. Analysis:—

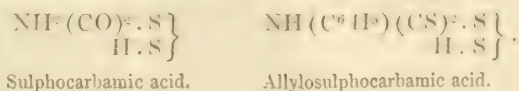
Nitrogen	..	1	=	14	1.00
Carbon	6.89	8		48	6.78
Hydrogen	1.90	12		12	1.69
Iodine	89.05	5		635	89.56

Deciodide of Tetramethylammonium, $C^8 H^{12} NI^{10}$, is produced by adding iodine to a boiling solution of pentiodide of tetramethylammonium in dilute alcohol. It forms a melted mass below the boiling fluid, and crystallizes on cooling: it gives off vapours of iodine in the air, and contains 95.35 per cent. of iodine.

From this it appears that these periodides are only formed by the tetra compounds of the conjugate ammonias (those in which 4 atoms of hydrogen of the ammonia are replaced by hydrocarbons), the compounds of which are not volatile, and of which the hydrated oxides have a great similarity with hydrate of potash. The solution of iodine in iodide of potassium perhaps also contains such periodides.—Liebig's *Annalen*, xci. p. 33.

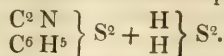
On some double Compounds of Oil of Mustard. By H. WILL.

In my investigation of the essential oil of black mustard*, I ascertained the existence of a compound of oil of mustard with sulphuretted hydrogen, of the formula $C^8 H^5 NS^2, H^2 S^2$. This compound has been called *sulphosinapic acid* by L. Gmelin; Gerhardt regards it as sulphocarbamic acid, in which 1 equiv. of hydrogen is replaced by the radical allyle:—

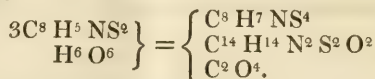


* Chem. Gaz., vol. iii. pp. 253 and 277.

According to the formula proposed by me for this body, it would be sulphocyanide of allyle combined with sulphuretted hydrogen:—



I obtained it formerly by the action of an alcoholic solution of potash upon oil of mustard, when it is produced together with carbonic acid and the oleaginous body $\text{C}^{14} \text{H}^{14} \text{N}^2 \text{S}^2 \text{O}^2$, in accordance with the equation—



After the separation of the oleaginous body from the solution much diluted with water, and the neutralization of the latter with acetic acid, acetate of lead throws down a very changeable lead-salt, of a citron-yellow colour, the analysis of which led to the formula $\text{C}^6 \text{H}^5 \text{NS}^2 + \left. \begin{array}{l} \text{HS} \\ \text{PbS} \end{array} \right\}$.

I found that the whole of the oil of mustard might be readily converted into this sulpho-acid, when it is brought directly into contact with alcoholic solutions of the metallic hydrosulphurets. The analysis of the compounds hereafter described, and prepared in this manner, shows that the composition previously deduced by me from the lead-salt is the correct one.

Double Sulphide of Oil of Mustard and Ammonium, $\text{C}^8 \text{H}^{10} \text{N}^2 \text{S}^4 = \left. \begin{array}{l} \text{C}^2 \text{N} \\ \text{C}^6 \text{H}^5 \end{array} \right\} \text{S}^2 + \left. \begin{array}{l} \text{H} \\ \text{NH}^4 \end{array} \right\} \text{S}^2$.—If oil of mustard be dropped into a saturated and colourless solution of sulphuretted hydrogen and sulphide of ammonium in strong alcohol, the odour of the former immediately disappears, the fluid becomes strongly heated, and in a few moments sets into a gelatinous mass of colourless laminæ. For analysis the substance was dried *in vacuo*; it gave,—

	Found.				Calculated.
	I.	II.			
Carbon	31.70	31.36	8	= 48	32.00
Hydrogen	6.90	6.77	10	10	6.66
Nitrogen	17.40	..	2	28	18.67
Sulphur	43.03	43.30	4	64	42.67

The salt is rather unstable; it decomposes by keeping, like the following compounds.

Double Sulphide of Oil of Mustard and Potassium, $\text{C}^8 \text{H}^6 \text{NS}^4 \text{K} = \left. \begin{array}{l} \text{C}^2 \text{N} \\ \text{C}^6 \text{H}^5 \end{array} \right\} \text{S}^2 + \left. \begin{array}{l} \text{H} \\ \text{K} \end{array} \right\} \text{S}^2$.—An alcoholic, or even a watery solution of sulphuretted hydrogen and sulphuret of potassium, to which oil of mustard has been added as long as its odour disappears, furnishes by slow evaporation *in vacuo*, and in considerable quantities, large rhombic tables, often of an inch in diameter; when the solution is more rapidly evaporated, acicular crystals are formed. Whilst in the fluid they are transparent and colourless; in the air they become opaque and yellow, losing their form and their perfect solubility in

water, which then leaves a tough sulphur-yellow mass. The watery solution of the freshly-prepared salt may be heated without evolving any odour of oil of mustard; if nitrate of silver be added to the heated solution, the odour of oil of mustard is immediately produced, with precipitation of sulphuret of silver; oil of mustard is also evolved by heat from the dry compound.

1.2360 grm. of the air-dried salt furnished on analysis 0.621 grm. of sulphate of potash. 0.7825 grm. gave 2.161 grms. of sulphate of baryta, representing K 22.50 and S 38.09 per cent. The above formula requires K 22.90 and S 37.38 per cent.

Oil of Mustard and Sulphide of Potassium.—*a.* $C^8 H^5 NS^2 + 2KS$.

An alcoholic solution of sulphide of potassium mixed with oil of mustard, the former being a little in excess, deposits on gentle evaporation a white granular salt, which when heated evolves oil of mustard without changing its colour. Analysis gave,—

	Found.	Calculated.
Potassium	39.2	37.4

b. $C^8 H^5 NS^2 + KS$.

The mother-liquor from which the preceding salt had separated, when left standing *in vacuo* over sulphuric acid, furnished acicular crystals, of a scarcely yellowish colour, which behave like the preceding salt, but contain less potassium. Analysis:—

	Found.		Calculated.
	I.	II.	
Potassium	25.5	25.0	25.4

Oil of mustard consequently combines not only with sulphuretted hydrogen and metallic sulphides to form crystallizable salts, but also with the soluble simple sulphides, and even, as appears from the preceding analyses, in different proportions.

Double Sulphide of Oil of Mustard and Sodium, $C^8 H^5 NS^2$, $\left. \begin{matrix} Na \\ H \end{matrix} \right\} S^2 + 6HO$.—This compound is easily obtained by mixing a warm alcoholic solution of sulphuretted hydrogen and sulphide of sodium with oil of mustard as long as the odour of the latter disappears. It separates in pearly laminæ, which are fatty to the touch, and on being heated, first melt, and afterwards evolve an abundance of oil of mustard. The salt contains water of crystallization, and, like the preceding, cannot be kept without change. Analysis:—

	Found.				Calculated.
	I.	II.			
Carbon	23.70	..	8	= 48	23.90
Hydrogen	5.93	..	12	12	5.73
Nitrogen	..	..	1	14	
Sulphur	..	..	4	64	
Oxygen	..	..	6	48	
Sodium	11.00	11.4	1	23.1	11.10

Double Sulphide of Oil of Mustard and Barium, $C^8 H^5 NS^2$, $\left. \begin{matrix} Ba \\ H \end{matrix} \right\} S^2 + 4HO$.—This salt is produced by heating oil of mustard with a solution of sulphide of barium saturated with sulphuretted hydrogen and mixed with a little alcohol, or by diffusing oil of mustard and hydrate of baryta in water, and introducing sulphuretted hydrogen with an addition of alcohol; it is also deposited from the mother-liquor of the salt, which is more difficult of solution in alcohol, the analysis of which is given hereafter, and which contains simple sulphide of barium. The very soluble salt forms laminar crystals, similar to those of the sodium compound. In the following analysis, I. represents a salt prepared by the first process, II. a salt deposited from the mother-liquor of the following compound:—

	Found.				Calculated.
	I.	II.			
Carbon	..	19.30	8	= 48	20.20
Hydrogen	..	4.60	10	10	4.23
Nitrogen	..	..	1	14	
Sulphur	..	26.5	4	64	27.05
Oxygen	..	..	4	32	
Barium	30.4	30.44	1	68.6	29.00

Oil of Mustard and Sulphide of Barium, $C^8 H^5 NS^2 + 2BaS + 2HO$.—If a hot yellow solution of sulphide of barium, as obtained by treating the crude sulphide with water, be gradually mixed with oil of mustard until the odour of the latter becomes permanent, colourless or slightly yellowish laminæ are obtained on the cooling of the filtered solution; these fall to a white powder when exposed to the air. The same compound is precipitated by alcohol. The salt has an odour of oil of mustard, does not melt when heated, and burns like tinder at a stronger heat. The salt, dried by repeated pressure between paper, was employed for analysis. It gave,—

	Found.		Calculated.
	I.	II.	
Barium	49.1	47.3	47.94

This compound appears to crystallize with different quantities of water, as a salt prepared at another time gave 41.6 per cent. of barium on analysis, which would correspond with the formula $C^8 H^5 NS^2, 2BaS + 6HO$ (calc. 42.6 Ba).

Double Sulphide of Oil of Mustard and Calcium.—If milk of lime be mixed with oil of mustard and a little alcohol to effect the solution of the latter, the odour disappears entirely on the saturation of the mixture with sulphuretted hydrogen. A clear solution is obtained; and this, on evaporation in the water-bath, leaves the calcium compound in the form of a slightly yellowish transparent jelly. When completely dried, it is decomposed, with an abundant evolution of oil of mustard.—Liebig's *Annalen*, xcii. p. 59.

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No. CCXCIX.—April 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Remarks on the Theoretical Views of the Constitution of Organic Substances. By HEINRICH WILL.

[Concluded from page 109.]

THE hydrates of the monobasic organic acids and their æthers will serve to show the influence exercised upon the boiling-point by the replacement of the second atom of hydrogen, with alteration of the volume-equivalent. These substances may be regarded either as $C^{2n} H^{2n-1} O^2 \cdot O + HO$, or, according to Gerhardt and Williamson, as $C^{2n} H^{2n-1} O^2 \left\{ \begin{smallmatrix} H \\ H \end{smallmatrix} \right\} O^2$; it is in both cases certain, that in the space

occupied by water, whether $HO + HO$ or $\left\{ \begin{smallmatrix} H \\ H \end{smallmatrix} \right\} O^2$, one equivalent of hydrogen is replaced by an equivalent of an acid radical, while in the æthers of these acids the second equivalent of hydrogen is replaced by an alcohol radical, without alteration of the volume-equivalent. It is indifferent whether the formula adopted for these æthers is $C^{2n} H^{2n-1} O^2 \cdot O + C^{2n} H^{2n+1} O$ or $\left\{ \begin{smallmatrix} C^{2n} H^{2n-1} O^2 \\ C^{2n} H^{2n+1} \end{smallmatrix} \right\} O^2$:—

	Formulae.	Boiling-points.	Differences.
<i>Formic acid</i>	$C^2 \begin{smallmatrix} HO^2 \\ H \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	212° F.	
Formiate of methyle ..	$C^2 \begin{smallmatrix} HO^2 \\ H^3 \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	94·8	117·2
Formiate of æthyle	$C^2 \begin{smallmatrix} HO^2 \\ C^4 H^5 \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	131	81
Acetic acid	$C^2 \begin{smallmatrix} C^2 H^3 O^2 \\ H \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	248	
Acetate of methyle	$C^2 \begin{smallmatrix} C^2 H^3 O^2 \\ C^2 H^3 \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	131	117
Acetate of æthyle	$C^2 \begin{smallmatrix} C^2 H^3 O^2 \\ C^4 H^5 \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	165·2	82·8
Butyric acid	$C^2 \begin{smallmatrix} C^6 H^7 O^2 \\ H \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	312·8	
Butyrate of methyle ..	$C^2 \begin{smallmatrix} C^6 H^7 O^2 \\ C^2 H^3 \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	199·4	113·4
Butyrate of æthyle	$C^2 \begin{smallmatrix} C^6 H^7 O^2 \\ C^4 H^5 \end{smallmatrix} \left\{ \begin{smallmatrix} \\ \\ \end{smallmatrix} \right\} O^2$	233·6	79·2

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	Formulae.	Boiling-points.	Differences.
Valerianic acid	$\left. \begin{array}{l} \text{C}^2 \text{C}^8 \text{H}^9 \text{O}^2 \\ \text{H} \end{array} \right\} \text{O}^2$	347° F.	
Valerate of methyle ..	$\left. \begin{array}{l} \text{C}^2 \text{C}^8 \text{H}^9 \text{O}^2 \\ \text{C}^2 \text{H}^3 \end{array} \right\} \text{O}^2$	233·6	113·4
Valerate of æthyle	$\left. \begin{array}{l} \text{C}^2 \text{C}^8 \text{H}^9 \text{O}^2 \\ \text{C}^4 \text{H}^5 \end{array} \right\} \text{O}^2$	267·8	79·2

The uniformity in the differences of the boiling-points of the hydrated acids, as well as of their methyl- and æthylæthers, shows that the boiling-point of these related substances is determined by the position of that hydrogen which is replaced by the alcohol radical. When this substitution takes place in the acid- or alcohol radical itself, the boiling-point is raised about 37 degrees for each equivalent of methyle, as in all truly homologous substances. When, on the contrary, the basic equivalent of hydrogen, which in the hydrated acids performs the functions of a radical, is replaced by methyle, the boiling-point is lowered; this reduction is constant, amounting to about 117°, the reduction of the boiling-point by æthyle being about 80° (=117-37). Regarding the æthers as substances whose volume-equivalents are equal, and the same as those of alcohols—and in the case of the æthers obtained by Williamson no other view can be entertained—it appears, on comparing the boiling-points of the æthers with those of the alcohols, that the same uniformity obtains as in the case of the boiling-points of the hydrated acids and their compound æthers; an equivalent of methyle lowers the boiling-point of alcohols about 117° when it replaces the hydrogen existing in alcohol as a simple element; an equivalent of æthyle lowers the boiling about 80 degrees:—

	Formulae.	Boiling-points.	Differences.
Æthylalcohol	$\left. \begin{array}{l} \text{C}^4 \text{H}^5 \\ \text{H} \end{array} \right\} \text{O}^2$	173°·3 F.	
Æthylomethylæther	$\left. \begin{array}{l} \text{C}^4 \text{H}^5 \\ \text{C}^2 \text{H}^3 \end{array} \right\} \text{O}^2$	51°·8	— 121·5
Æthylæther.	$\left. \begin{array}{l} \text{C}^4 \text{H}^5 \\ \text{C}^4 \text{H}^5 \end{array} \right\} \text{O}^2$	95°·9	— 77·4

There is the same difference between these boiling-points as between those of the hydrated acids and their æthers, both of which have the same volume-equivalents. The difference between the boiling-point of methylalcohol and æthylomethylæther is 88 degrees (140°-51·8). So likewise in,—

	Formulae.	Boiling-points.	Differences.
Amylalcohol	$\left. \begin{array}{l} \text{C}^{10} \text{H}^{11} \\ \text{H} \end{array} \right\} \text{O}^2$	269°·6 F.	
Amylomethylæther ..	$\left. \begin{array}{l} \text{C}^{10} \text{H}^{11} \\ \text{C}^2 \text{H}^3 \end{array} \right\} \text{O}^2$	197°·6	— 72
Amoloæthylæther. . . .	$\left. \begin{array}{l} \text{C}^{10} \text{H}^{11} \\ \text{C}^4 \text{H}^5 \end{array} \right\} \text{O}^2$	233°·6	— 36

an equivalent of methyle reduces the boiling-point of amylalcohol 72° , an equivalent of æthyle 37° .

When either methylalcohol (boiling at 140°) or æthylalcohol (boiling at $173^{\circ}\cdot3$) is taken as the standard for comparison, it will be seen that amyle exercises the same influence upon the boiling-point in both æthers (raising it 58°); the same number expresses the difference between the boiling-points of water and amylalcohol. The boiling-points of æthers which contain the radicals butyle (C^8H^9) or caproyle ($C^{12}H^{13}$), besides the radicals methyle or æthyle, will render more prominent the influence exercised upon the boiling-points of substances by two radicals whose functions in this respect differ in such a manner that, both in alcohol and æther, the one tends to reduce the boiling-point while the other tends to raise it. But the instances already brought forward suffice to show the uniform relation between the boiling-points of alcohols and æthers; they show that the proximate cause of the apparently contradictory differences between the boiling-points of alcohols and æthers, hydrated acids and their æthers, is to be sought in the position of the substituted radical and the volume which it occupies; a consideration of these relations furnishes an explanation of the circumstance, that metameric substances, such as compound æthers and hydrated acids, alcohols and æthers, have such different boiling-points.

A similar relation appears to obtain in the influence exercised upon the boiling-point by the position of the alcohol radicals replacing hydrogen in the volatile organic bases. Thus, from the boiling-points of the following series of volatile bases, some members of which are metameric, it may be inferred that they are homologous in the sense expressed by the formulæ:—

	Boiling- points.	Differ- ences.		Boiling- points.	Differ- ences.
Pyridine.			Aniline.		
$C^{10}H^3$ H H } N	239°		$C^{12}H^5$ H H } N	$359^{\circ}\cdot6$	
Picoline.			Toluidine.		
$C^{10}H^2(C^2H^3)$ H H } N	272°	$+33^{\circ}$	$C^{12}H^4(C^2H^3)$ H H } N	$362^{\circ}\cdot4$	$+28^{\circ}\cdot8$
Lutidine.			Xylidine.		
$C^{10}H^2(C^4H^5)$ H H } N	309°	$+70$	$C^{12}H^4(C^4H^5)$ H H } N		?
			Cumidine.		
			$C^{12}H^4(C^6H^7)$ H H } N	$137^{\circ}\cdot0$	$+77^{\circ}\cdot4$

For the series whose initial member is pyridine, it remains to ascertain experimentally whether the individual members contain

two other replaceable atoms of hydrogen; Morley and Abel have recently shown that toluidine, like aniline, is an amine base, and this may likewise be assumed with regard to xyldine and cumidine, from the analogy in the mode of their formation. It may also be inferred hence, that, in the hydrocarbons homologous with benzole, $C^{12}H^5$, H, it is not the hydrogen without the phenyle which is replaced by a radical, that therefore toluole is $C^{12}H^4(C^2H^3)$, H, &c.

In the substitution-derivatives of aniline obtained by Hofmann, some of which are metameric with the above-mentioned bases, the uniformities which obtain in the differences of the boiling-points are of another kind; and this is likewise the case with the æthylated and methylated modifications of piperidine described by Cahours:—

Aniline.	Boiling-points.	Differences.	Piperidine.	Boiling-points.	Differences.
$C^{12}H^5$ H H } N	359°·6		$C^{10}H^9$ H H } N	222°·8	
Methylaniline.			Methylpiperidine.		
$C^{12}H^5$ C^2H^3 H } N	377°·6 + 18·0		$C^{10}H^9$ C^2H^3 H } N	242°·6	+ 19·8
Æthylaniline.			Æthylpiperidine.		
$C^{12}H^5$ C^4H^5 H } N	399°·2 + 39·6		$C^{10}H^9$ C^4H^5 H } N	262°·4	+ 39·6

It appears from this that an equivalent of methyle raises the boiling-point about 18 degrees above that of the initial member of the series, and that an equivalent of æthyle raises it about 36 degrees when replacing the hydrogen existing as a simple element in aniline or piperidine, while, on the contrary, when the hydrogen existing as part of a compound element is replaced, the incremental influence upon the boiling-point is for methyle 36 degrees and for æthyle 72 degrees. The boiling-point of æthyltoluidine is likewise accordant with this view:—

Toluidine.	Boiling-point.	Æthyltoluidine.	Boiling-point.	Difference.
$C^{12}H^4(C^2H^3)$ H H } N	388°·4 F.	$C^{12}H^4(C^2H^3)$ C^4H^5 H } N	422°·6 F.	+ 34°·2

Consequently the boiling-point of methyltoluidine ought to be about 226°·4 F.

The incremental influence exercised upon the boiling-point when the third equivalent of hydrogen is replaced either in aniline or toluidine by an alcohol radical is again less, and it appears uniform:—

Boiling- points.	Differ- ences.	Boiling- points.	Differ- ences.
Æthylaniline. $\left. \begin{array}{l} \text{C}^{12}\text{H}^5 \\ \text{C}^4 \text{H}^5 \\ \text{H} \end{array} \right\} \text{N}$	399°·2 F.	Æthyltoluidine. $\left. \begin{array}{l} \text{C}^{12}\text{H}^4(\text{C}^2\text{H}^3) \\ \text{C}^4 \text{H}^5 \\ \text{H} \end{array} \right\} \text{N}$	422°·6 F.
Diæthylaniline. $\left. \begin{array}{l} \text{C}^{12}\text{H}^5 \\ \text{C}^4 \text{H}^5 \\ \text{C}^4 \text{H}^5 \end{array} \right\} \text{N}$	416°·3 F. + 17°·1	Diæthyltoluidine. $\left. \begin{array}{l} \text{C}^{12}\text{H}^4(\text{C}^2\text{H}^3) \\ \text{C}^4 \text{H}^5 \\ \text{C}^4 \text{H}^5 \end{array} \right\} \text{N}$	442°·0 F. + 19°·4

While the first equivalent of æthyle raises the boiling-point about 36, the second equivalent raises it only about 30 degrees. The boiling-points of aniline (359°·6) and amylaniline (496°·4), of piperidine (366°·8) and amylpiperidine, differ to nearly the same amount (222°·8). The influence exercised upon the boiling-point in volatile bases which contain only alcohol radicals having the general formula $\text{C}^{2n}\text{H}^{2n+1}$, likewise appears to be uniform, as in the case of æthylamine (66°·2) and diæthylamine (134°·6), the difference being 68·4 degrees ($= 34\cdot2 \times 2$).

The facts that have already been ascertained are by no means adequate to furnish an exact knowledge of the influence exercised upon the boiling-point of volatile organic substances by the substitution of methyle for hydrogen; but it follows with certainty from the uniformities already pointed out, that the reason why the introduction of methyle into a substance is accompanied sometimes by an increment and sometimes by a depression of the boiling-point, is to be sought in the different position of the replaced hydrogen and its different relation of volume in the original substance. This difference of position and volume determines a change of chemical functions within certain limits, and likewise a uniform change of physical functions, which becomes perceptible in the boiling-point. It is moreover evident that the direction and amount of this change are also dependent, not only upon the position or the atomic weight of the replacing radical, but likewise upon its composition, that is, the relative proportion of carbon and hydrogen atoms.

As the boiling-point of hydrated formic acid is the same, or nearly the same, as that of water, it may be assumed, from the comparison of H^2O^2 with $\left. \begin{array}{l} \text{C}^2\text{HO}^2 \\ \text{H} \end{array} \right\} \text{O}^2$, that the radical formyle C^2HO^2 exercises the same influence upon the boiling-point as hydrogen itself, and that the anhydride of formic acid would have the same boiling-point as water or hydrated formic acid. The boiling-point of formic acid is raised when the hydrogen in formyle is replaced by methyle, and when, with production of acetyle, $\text{C}^2\text{C}^2\text{H}^3\text{O}^2$, formic acid is converted into acetic acid. If Gerhardt's opinion, that the anhydrides have the same relative condensation as the hydrates, it follows that the increment of the boiling-point of the anhydrides must bear some relation to the number of equivalents of methyle replacing the hydrogen in formyle.. This is indeed the case with acetic acid, and approximatively so for the higher acids:—

Hydrated formic acid.	Boiling- points.	Differ- ences.	Anhydrous formic acid.	Boiling- points.	Differ- ences.
$\left. \begin{array}{c} \text{C}^2\text{H}\text{O}^2 \\ \text{H} \end{array} \right\} \text{O}^2$	212° F.		$\left. \begin{array}{c} \text{C}^2\text{H}\text{O}^2 \\ \text{C}^2\text{H}\text{O}^2 \end{array} \right\} \text{O}^2$	212° F.?	
Hydrated acetic acid.			Anhydrous acetic acid.		
$\left. \begin{array}{c} \text{C}^2\text{C}^2\text{H}^3\text{O}^2 \\ \text{H} \end{array} \right\} \text{O}^2$	248°	+ 36°	$\left. \begin{array}{c} \text{C}^2\text{O}^2\text{H}^3\text{O}^2 \\ \text{C}^2\text{O}^2\text{H}^3\text{O}^2 \end{array} \right\} \text{O}^2$	278°·6	+ 66°·6
Hydrated butyric acid.			Anhydrous butyric acid.		
$\left. \begin{array}{c} \text{C}^2\text{C}^6\text{H}^7\text{O}^2 \\ \text{H} \end{array} \right\} \text{O}^2$	312°·8	+ 100°·8	$\left. \begin{array}{c} \text{C}^2\text{C}^6\text{H}^7\text{O}^2 \\ \text{C}^2\text{C}^6\text{H}^7\text{O}^2 \end{array} \right\} \text{O}^2$	374°	+ 162°
Hydrated valerianic acid.			Anhydrous valerianic acid.		
$\left. \begin{array}{c} \text{C}^2\text{C}^8\text{H}^9\text{O}^2 \\ \text{H} \end{array} \right\} \text{O}^2$	347°	+ 135°	$\left. \begin{array}{c} \text{C}^2\text{C}^8\text{H}^9\text{O}^2 \\ \text{C}^2\text{C}^8\text{H}^9\text{O}^2 \end{array} \right\} \text{O}^2$	419°	+ 207°

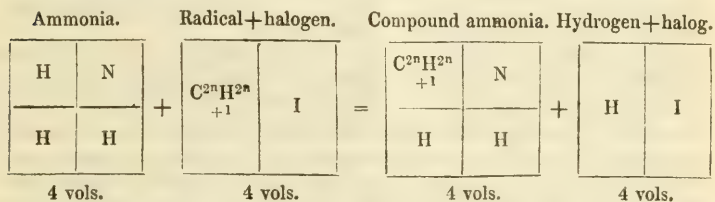
If anhydrous acetic acid were really $\text{C}^4\text{H}^3\text{O}^3$, it might, apart from the improbability of an uneven number of oxygen atoms and the discrepancy in the condensation, be maintained, as in the case of æther and alcohol, and with equal justice, that the boiling-point of the hydrated acid should be higher than that of the anhydride; while, in reality, the reverse is true. Anhydrous butyric acid, represented by the formula $\text{C}^8\text{H}^7\text{O}^3$, differs from anhydrous acetic acid, $\text{C}^4\text{H}^3\text{O}^3$, by $2\text{C}^2\text{H}^2$; consequently its boiling-point ought, in accordance with this view of their constitution, to be 350°·6 F. ($278^\circ\cdot6 + 36 \times 2$), and that of anhydrous valerianic acid 386°·6 F. ($278^\circ\cdot6 + 36 \times 3$). But experience shows that the influence exercised by a higher radical upon the boiling-point of a substance never exceeds the calculated limit, but generally falls short of it. Thus the boiling-point of caproic acid, containing 12 atoms of carbon, does not present such an exact conformity with calculation as the lower members of the same series of acids; and it cannot therefore be wondered that anhydrous butyric acid, containing, with equality of volume, 16 atoms of carbon, should have a somewhat lower boiling-point than would be assigned to it by theory.

When, in the endeavour to ascertain the constitution of volatile organic substances, and particularly those whose equivalents are still disputed, the uniformities that obtain in their boiling-points and relations of condensation are adequately considered, there is scarcely any doubt but that the formulæ proposed by Gerhardt and Williamson for æther and the so-called anhydrous acids must be adopted.

It may be that at present there is a tendency to exceed the boundaries of applicability of a view which has so happily united two theories, that of substitution and that of radicals, which were once so antagonistic, though now recognized by all chemists as equally true; but still it cannot be denied that under its influence the basis is being laid for a reform in organic chemistry, which must likewise extend to inorganic chemistry, since the laws of combination

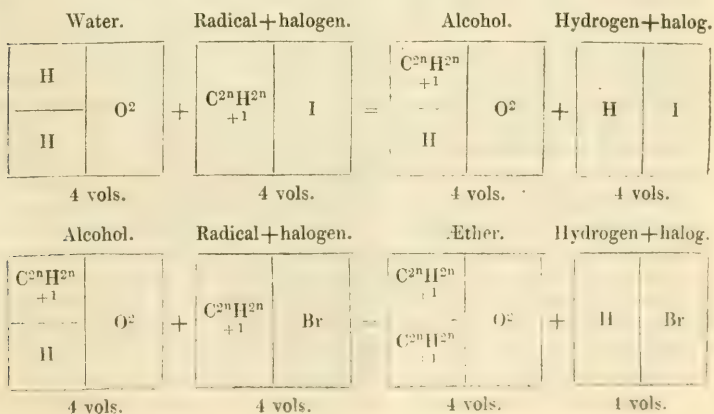
obtain equally for all elements. Natural laws always acquire a simplicity in expression when accurately known, and it is precisely the simplicity of this view, which does not present any discrepancies between its logical consequences and either the physical or chemical relations of organic substances, that constitutes, if not a demonstration of its truth, at least a strong argument for its probability.

There is but one view entertained as to the constitution of the volatile organic bases prepared by Wurtz and Hofmann; from their mode of formation, from their general physical and chemical characters, no doubt is entertained that these bases have a common type, ammonia, from which they are derived by substitution of alcohol radicals for hydrogen without any change in the volume of the original substance:—



This process may be repeated, without alteration of volume, until all the hydrogen atoms (existing as simple elements) in ammonia are replaced by radicals. The haloid compounds of acid radicals replace in a similar manner the hydrogen of ammonia by an acid radical.

The formation of an alcohol from water and the haloid compound of an alcohol radical, the formation of an æther from an alcohol and the haloid compound of an alcohol radical, or the formation of a compound æther from an alcohol and the haloid compound of an acid radical, are altogether and in every respect analogous to the formation of compound ammonias:—



known to be dependent upon the capability of carbon to combine with hydrogen, oxygen or nitrogen, forming series of compound elements which possess essentially the chemical nature of the metalloid hydrogen, and probably also the same relations of volume; indeed these compound elements combine, forming others still more complex and possessing analogous characters. From these series of analogous elements are derived series of analogous compounds, which present much more accessible points of comparison than similar inorganic substances. These series afford, especially in the case of volatile substances, the material for estimating step by step the influence which presents itself in the alteration of the characters of the substance, as the result of a parallel alteration of the characters of the radical.

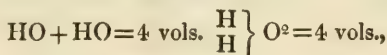
From this point of view, the result of the question as to the constitution and the equivalent of æther and anhydrous acids, is decidedly favourable to the views held by Gerhardt and Williamson.

Whether the constitution of a monobasic organic acid is regarded as representible by the formulæ $C^{2n} H^{2n-1} O^3 + HO$ or $C^{2n} H^{2n+1} C^2$, $O^3 + HO$, or $C^{2n} H^{2n+1} C^2 O^2$, O , HO , or $\left. \begin{matrix} C^2 C^{2n} H^{2n+1} O^2 \\ H \end{matrix} \right\} O^2$, it is certain that the space occupied by the vapour of an equivalent of the substance formed by the substitution of an alcohol radical for the basic molecule of hydrogen remains unaltered; the compound æther presents the same condensation as the hydrated acid, whether the position of the molecule is represented by the formulæ $C^{2n} H^{2n-1} O^3 + C^{2n} H^{2n+1} O$, or $C^{2n} H^{2n+1} C^2$, $O^3 + C^{2n} H^{2n+1} O$, or $C^{2n} H^{2n+1} C^2 O^2$, $O + C^{2n} H^{2n+1} O$, or $\left. \begin{matrix} C^2 C^{2n} H^{2n+1} O^2 \\ C^{2n} H^{2n+1} \end{matrix} \right\} O^2$. It is quite as certain that the differences between the boiling-points of the hydrated acids and those of their compound æthers with a lower radical, are the same as the differences between the boiling-points of the alcohols and those of the æthers with a lower radical. Moreover, when it is found that all the other circumstances admitted to furnish data for determining the constitution of a substance are in favour of an alteration of the formula, as in the case of the æthers, the existence of analogous substances, with regard to whose equivalents and the arrangement of their atoms there is scarcely any doubt whatever, whose modes of formation and decomposition are identical, it remains to be shown upon what grounds the formula $C^4 H^5 O$ should be retained for wine æther, while the duplicate formula corresponds with all the above requirements.

The formulæ $C^4 H^5 O$, $C^2 H^3 O$ or $C^{10} H^{11} O$, $C^3 H^3 O$, for the æthers obtained by Williamson, do not present any discrepancy when inorganic substances are taken as the standard of comparison, although the formula $C^4 H^5 O$, $C^4 H^5 O$ would do so, because it implies a possibility of the combination of two perfectly similar molecules to a complete whole. The formula $C^4 H^5 O$ is only in part reconcileable with the above-mentioned uniformity in the relations of weight between the elements, while the formula $\left. \begin{matrix} C^4 H^5 \\ C^4 H^5 \end{matrix} \right\} O^2$ is recon-

cileable with the relations both of weight and volume presented by volatile organic substances, as well as the differences between the boiling-points of substances comparable with each other. This is likewise true of the anhydrous acids obtained by Gerhardt.

Kolbe has put forward the electrolytic decomposition of monobasic organic acids having the formula $C^{2n}H^{2n}O^1$, as an incontrovertible proof of the incorrectness of the opinion that these acids should be regarded as water, H^2O^2 , in which an equivalent of hydrogen is replaced by an acid radical. Formerly they were regarded by Kolbe as hydrates of a higher oxide of the conjugate radical $C^{2n}H^{2n+1}$, C^2 , acetic acid for example, as C^2H^3 , $C^2O^1 + HO$; but now he considers the existence, in the series of acids in question, of a radical containing oxygen ($C^{2n}H^{2n+1}$, C^2O^2) as proved. The question therefore turns upon the existence or non-existence of water in these acids, whether or not they are hydrates, that is, compounds of two independent groups of atoms, as would be represented respectively by the following formulæ:—



or



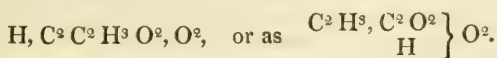
Kolbe's experiments show, that in the decomposition of these acids by electrolysis, hydrogen is evolved at the negative pole, while the radical $C^{2n}H^{2n+1}$ is evolved together with carbonic acid at the positive pole. It is easily perceptible, that whichever of the above formulæ are adopted, the hydrogen and the radical molecules occupy the same position with regard to the oxygen not contained in the radical; the result of the electrolytic decomposition cannot be in any way influenced either by the altered atomic weight of oxygen or the position of the atoms, which differs only inasmuch as one formula represents both molecules of the radical as combined with a single (indivisible) molecule of oxygen, while the other represents the radical and the hydrogen combined with a molecule of oxygen. Any argument drawn from the electrolytic decomposition of the acids in question against the one mode of representation must necessarily have equal weight against the other.

Undoubtedly the transposition of the molecules of organic substances effected by electrolysis is to be regarded as furnishing important data for the determination of their original arrangement, and Kolbe has with justice directed particular attention to this. It was not hitherto possible to obtain, by merely chemical methods, so adequate a proof of the constitution of the acids generally as is presented by the electrolytic decomposition of these substances or their salts.

From the solution of a salt containing a metal that does not decompose water, the metal is always eliminated, under the influence of an electrical current at the negative pole, in a free state, and not as oxide. From solutions of alkaline salts a quantity of hydrogen

is evolved which is equal to that evolved from a hydrogen compound, and equivalent to the metal separated from a metallic salt by the same amount of electricity. It is inferred hence, that the hydrogen which is evolved during the electrolytic decomposition of a salt containing an alkaline metal originates from a secondary decomposition of water by the alkaline metal eliminated in the first instance, and that this metal exists in the salt, not as an oxide, but as the substitute for the basic hydrogen of the acid. Accordingly the acids are *hydrides*, and do not contain water; *they are not hydrates*.

If this mode of decomposition of salts by electrolysis is admitted to furnish any decisive evidence in reference to the chemical arrangement of atoms in substances, it is evident that in the monobasic organic acids the arrangement of the molecules should not be represented by the formula $C^{2n}H^{2n+1}C^2O^2, O+HO$; and if the existence in these acids of an acid radical having the above general expression is admitted, the view maintained by Gerhardt and Williamson follows as a necessary consequence, for there is then no longer any reason to believe that the two oxygen atoms—represented in the above formula as combined on the one hand with the radical, on the other with the hydrogen—are isolated. It is then indifferent, as regards the mode of decomposition of these acids by electrolysis or otherwise, whether the basic equivalent of hydrogen, occupying an independent space in the substance, is placed in the formula before or under the acid radical; whether, for example, the formula for acetic acid is written as



The alteration of the atomic weights of oxygen and carbon in the manner proposed by Gerhardt, does not in any way affect the facts of the case, although by this means the formulæ are rendered more simple and—if the indivisibility of the oxygen molecule ($O=16$) and of the carbon molecule ($C=12$) is admitted—more correct.

The objections which may be derived from the composition of salts containing a metallic oxide having the formula M^2O^3 , have no special reference to the theory of the constitution of organic acids, but affect generally that of all acids. Their satisfactory explanation is attended with the same difficulties whether the salts are regarded as containing oxides or metals, and the decision of the question whether or not all acids are hydrides, cannot be in any sort dependent upon the uncertain atomic constitution of oxides having the formula M^2O^3 ; but it is probable the final solution of this problem will render another expression for the composition of the sesquioxides necessary.

To say that an equivalent of potash (containing 1 equiv. of metal) replaces an equivalent of protoxide containing 1 equiv. of metal in a protosalt of iron, while 3 equivs. of potash (containing 3 equivs. of metal) replace only 1 equiv. of sesquioxide of iron (containing 2 equivs. of metal) in a persalt of iron, is indeed not less an infraction of the theory of equivalents—of chemical substitution in definite

and constant proportions by weight—than to assume that an equivalent of potassium = 39.2 or an equivalent of hydrogen = 1 have in relation to protosalts of iron the same chemical value as 28 iron, while in relation to persalts they are respectively equivalent to 18.66 iron ($\frac{2}{3} \times 28$). The reality of the chemical equivalence of one and the same quantity, by weight, of a metal, of potassium, or of hydrogen, and different quantities of another metal, as iron, is unquestionable, although the interpretation is not. In the same way that iron presents, in respect to the same quantity of another element, equal chemical value, according to its state of combination, sometimes in the proportion by weight of 28 (O=8), sometimes in that of 18.66; so the same amount of electricity which eliminates from a potassium compound 39.2 parts by weight of potassium (or 1 part of hydrogen), from a silver compound 108 parts of silver, from a protosalt of iron 28 parts of iron,—would eliminate from a sesquisalt of iron only 18.66 parts of iron; indeed this appears the only possible result when it is remembered that *one equivalent* of the radical (or the acid) is in reality combined in the sesquisalts, not with 28 parts, but with 18.66 parts of metal.

There is every reason to assume that the equivalence and arrangement of the atoms of monobasic organic acids is better understood than those of the sesquioxides; for while the equivalents of these organic substances may be determined with the same precision as that of any inorganic substance of definite chemical character, they are at the same time, in virtue of their volatility and the diversity of ways in which their molecules may be transposed, as it were chemically transparent; they admit of penetration into their intimate construction and the arrangement of parts, furnishing from time to time fresh results, which unmistakeably point out that the modes of combination recognized in inorganic chemistry can no longer serve as a model of those in organic chemistry.—Liebig's *Annalen* for September 1854, p. 257.

On Mangostine. By Dr. W. SCHMID.

The mangostine tree (*Garcinia mangostana*), which is cultivated on the East Indian Islands, furnishes a fruit which is said to possess the most agreeable flavour of all tropical fruits. It is of the form of a berry and the size of an orange. Dr. Waitz, a surgeon in the Dutch East Indies, has employed the husk of the mango in fevers, and states that it is not only equal to bark, but even excels this when used in the fresh state. The author has accordingly examined these husks.

The husks used were dry, of a brownish-red colour, thick and spongy, with an astringent taste, and contained internally a yellow, semicrystalline substance. They were finely powdered, and repeatedly extracted with water.

The watery solution contained for the most part a tannin, which produced a black colour with iron. The residue was treated with hot alcohol, which completely dissolved the yellow crystalline

matter. The fluid was filtered and left standing, when a yellow amorphous mass separated on evaporation; this contained the body to which the author gives the name of *mangostine*, mixed with resin. The latter is very difficult of separation; the best method is to heat the filtered alcoholic solution to boiling, and add distilled water in small quantities until the fluid becomes opalescent. The resin, which is but sparingly soluble in cold dilute alcohol, is deposited on cooling; the mangostine does not separate until long afterwards, when it takes the form of small, yellow, silky laminæ; so that by pouring the fluid from the deposit of resin, the mangostine may be obtained tolerably pure. To purify it further, it is dissolved in alcohol, and precipitated with basic acetate of lead. The precipitate is well washed, suspended in alcohol, and decomposed whilst hot by sulphuretted hydrogen. The filtered solution is then mixed with water whilst boiling until it becomes milky, as the mangostine only crystallizes from a dilute alcoholic solution. The complete purification of the substance is completed by repeated crystallization from alcohol.

Mangostine crystallizes in thin laminæ, of a fine golden lustre; it is tasteless and inodorous; melts at about 374° F. without loss of water, forming a thick, transparent, deep yellow fluid, which solidifies on cooling into a brittle, amorphous, transparent mass; it is heavier than water. When heated above its melting-point, it is for the most part decomposed, but a part sublimes unchanged. It burns on platinum foil without residue. It is insoluble in water, but dissolves readily in alcohol and æther. The solutions have no reaction on litmus-paper.

Dilute acids dissolve the greater part of it with the aid of a moderate heat, and deposit it again unchanged on cooling. Concentrated nitric acid converts it into oxalic acid at an elevated temperature. Cold concentrated sulphuric acid dissolves it with partial decomposition, and with a dark yellowish-red colour; when heated, carbonization commences. It dissolves in alkalis with a yellow or brownish colour. It is not precipitated by metallic salts, with the exception of basic acetate of lead. It reduces the oxides of the noble metals. With chloride of iron it produces a greenish-black colour, which disappears on the addition of acids. Analysis led to the formula $C^{40} H^{32} O^{10}$:—

	I.	II.	III.			
Carbon	69.64	69.63	69.74	40	3000	70.17
Hydrogen	6.66	6.37	6.44	22	275	6.43
Oxygen	23.70	24.00	23.82	10	1000	23.40

For the preparation of the compound of mangostine and oxide of lead, the substance was dissolved in alcohol, and then treated with an alcoholic solution of neutral acetate of lead in such a manner that all the mangostine was not precipitated by the addition of a small quantity of ammonia. The precipitate thus produced was gelatinous, yellow, insoluble in water, slightly soluble in alcohol,

and decomposable by acids. When dried at 212°F ., it could be pounded into a light yellowish-green powder, which when heated burnt away quietly without scintillation. Analysis led to the formula $2(\text{C}^{40}\text{H}^{22}\text{O}^{10}) + 5\text{PbO} + \text{HO}$:—

	Found.			Calculated.
Carbon	38.67	80	6000	38.37
Hydrogen	3.45	45	562.5	3.59
Oxygen	13.74	21	2100	13.46
Oxide of lead	44.14	5	6972.5	44.58

This lead compound is not always of the same composition, for in two analyses of a compound prepared at another time the author obtained 37.85 and 37.46 per cent. of oxide of lead.

Several other bodies, obtained from plants of the same natural family (*Guttiferae*) as the *Garcinia mangostana*, appear to possess a certain relation with mangostine, both in regard to their formulæ and chemical properties.

According to Johnston, gamboge obtained from *Garcinia gutta* has the formula $\text{C}^{40}\text{H}^{18}\text{O}^{21}$. From this it appeared probable that mangostine might be obtained by the oxidation of gamboge. The author accordingly treated the latter substance with hot concentrated nitric acid, and obtained a crystalline body which appeared to possess reactions exactly analogous to those of mangostine.

Indian-yellow (purree), which is said to be obtained from the deposit of camel's urine after the animals have eaten the fruit of *Mangostana mangifer*, consists principally of euxanthate of magnesia; the acid of this salt has the formula $\text{C}^{40}\text{H}^{16}\text{O}^{21}$. Hence it appears possible that both mangostine and gamboge may be converted into euxanthic acid by passing through living bodies.

From this the author was induced to make some experiments with euxanthic acid, from which it appeared that this acid is a conjugate compound. Thus if it be treated with concentrated nitric acid, and the fluid be poured into water, euxanthone separates. The fluid filtered from this substance has the property of reducing peroxide of copper dissolved in potash, a power possessed neither by euxanthic acid nor by euxanthone.—Liebig's *Annalen*, xciii. p. 83.

On Ursone, a new Substance from the Leaves of Arctostaphylos uva ursi. By H. TROMMSDORFF.

The author has prepared a new crystallizable substance from this plant, to which he gives the name of *ursone*. An alcoholic extract of the leaves was made, the watery solution of which was employed in the preparation of arbutine according to Kawalier's method. The green residue remaining after the solution of the extract in water was repeatedly washed with æther, then decocted with alcohol, and the alcoholic fluid filtered whilst boiling. On cooling, it deposited a substance in fine crystals.

This substance is most easily obtained by exhausting the coarsely powdered leaves of the plant with about an equal weight of æther, in Mohr's apparatus for extraction with æther. An abundant deposit of crystalline powder is found in the dark green ætherial extract; this is washed with æther and recrystallized from alcohol.

The substance forms fine, colourless, silky, acicular crystals; it is tasteless and inodorous, insoluble in water, dilute acids and alkalis, and difficult of solution in alcohol and æther. It fuses by heat into a colourless liquid, which solidifies on cooling, forming a transparent, amorphous, cracked mass. At a higher temperature it boils and volatilizes, apparently unchanged, forming a white sublimate on the cold sides of the vessel. In contact with the air, it burns completely, with a yellow smoky flame, without leaving any cinder. Concentrated solution of potash appears to have no action upon it either when hot or cold. Concentrated sulphuric acid gives it an orange-yellow colour, without dissolving it completely, although the liquid also assumes this colour; when heated, the colour passes to brown, and at last carbonization takes place with evolution of sulphurous acid. Fuming nitric acid dissolves the substance with a slight evolution of nitrous acid, forming a clear yellow fluid, from which a white body is deposited in abundance on the addition of water.—*Archiv der Pharm.*, lxxx. p. 274.

ANALYTICAL CHEMISTRY.

On the Determination of Bromine in Combination with Chlorine. By Dr. MOHR.

THE estimation of bromine is still always effected by an indirect method, namely, by determining the weight of a silver precipitate containing bromine, and ascertaining the quantity of chloride of silver corresponding with, or the amount of pure silver contained in it. The usual mode of operation consists in fusing the precipitate containing the bromine in a current of chlorine gas until it undergoes no further loss of weight, and ascertaining the amount of bromine from the loss. A modification of this process consists in completely reducing the mixed precipitate, heated to redness in a bulb-tube, by hydrogen gas; the bromine is then calculated from the weight of the dried precipitate and that of the silver obtained. Or the precipitate may be reduced with zinc; but this is rejected by Rose as inexact.

These operations are very troublesome; they require the calcination and evolution of gas to be continued for several hours, and can only be carried on with small quantities of substance, as otherwise the operations would last for days. Hence the analysis of a part is taken for the whole, and the chances of error are multiplied.

Fehling has introduced an essential improvement into the method.

He found that in the partial precipitation of compounds of chlorine and bromine, all the bromine is contained in the first precipitate; for although chlorine has a greater affinity for metals than bromine, bromide of silver is less soluble than chloride of silver; and as both are in some degree soluble in the chlorides of the alkaline metals, the decomposition takes place until all the bromine is precipitated. A long digestion and frequent agitation of the precipitate is consequently required for complete precipitation, when all the bromine will be found in the precipitate. I could not make out why Fehling avoided heating the precipitate in the fluid, as when the latter is sufficiently diluted and afterwards cooled, this must facilitate the decomposition. Fehling then treats a certain portion of the weighed precipitate with chlorine gas in the usual manner, in a bulb-tube.

To avoid this method, which is not only tiresome, but also easily leads to errors if undecomposed portions of bromide of silver remain enclosed, I have exactly reversed the processes. I weigh the pure silver required for the precipitation, and employ the whole of it. Then by determining the weight of the precipitate obtained, I have all the data for the calculation of the bromine.

A quantity of silver is weighed sufficient to precipitate not only the whole of the bromine, but also some of the chlorine; this is put into a flask, and dissolved in dilute nitric acid; the fluid containing the bromine is then added to it. The whole is left standing for twenty-four hours, with frequent shaking, when the weight of the precipitate is determined. I prefer doing this without filtration, as silver precipitates settle very readily and completely, and the fluid may be decanted or drawn off with a siphon. A glass siphon, with several inches of india-rubber tube at the end of the long limb, will draw off the fluid to the last drop; towards the end the india-rubber tube may be compressed so as to reduce the stream to drops. The precipitate is then dried in a flask, which must be weighed previously, the air being changed by suction, or by means of a small pair of bellows. The weight of the dried and half-fused precipitate is then ascertained, and the weight of the silver contained in it being known, the quantity of bromine is calculated from these data.

I first employed this method in the determination of the bromine in the mother-liquor of the brine-springs near Kreuznach.

20 grms. of the mother-liquor were diluted with distilled water, and mixed with a freshly-prepared solution of 3 grms. of pure silver. The entire precipitate weighed 4.057 grms.; had it been pure chloride of silver, it could only have weighed 3.9849 grms.; bromine therefore was present, for the reactions showed that there was no iodine. The difference between the mixed precipitate and pure chloride of silver was not obtained in the bulb-tube, but calculated from the silver; it amounted to 0.0721 gm., and this multiplied by 1.796*, gives 0.1294916 gm. of bromine in 20 grms. of mother-liquor, or 0.647458 per cent. The entire amount of chlorine may now be thrown down from the filtrate by an excess of silver.

* See Rose's Handbuch, vol. ii. p. 602.

The amount of chlorine and bromine in the first precipitate was $4.057 - 3 = 1.057$ grm.; and as the bromine weighed 0.1291916 grm., the chlorine amounted to 0.9275 . The complete precipitation of the chlorine gave 12.759 grms. of chloride of silver $= 3.1662$ grms. chlorine; the addition of the above quantity to this makes 4.0897 grms. $= 20.448$ per cent. of chlorine.

The silver may also be employed in a standard solution, and the fluid completely precipitated. If the weight of the entire precipitate be then determined, we get all the data for the calculation of the bromine.

I employ the silver in a solution ten times more diluted than the ordinary reagents, that is to say, instead of dissolving 108 grms. (the equivalent of silver in grammes) in 1 litre, I dissolve 10.8 grms. of pure silver in nitric acid, and dilute this to 1 litre, or 17 grms. of pure nitrate of silver may be dissolved to form the same quantity of solution. Of this fluid, 1 cub. centim. represents one ten-thousandth of an atomic weight of any chlorine or bromine compound. In this manner tables may be prepared beforehand for all the substances referred to.

5 cub. centims. of mother-liquor $= 6.6975$ grms., were completely precipitated by the above normal solution of silver, with the assistance of heat and shaking, until the last drops no longer produced a precipitate. 140 cub. centims. were required, containing 1.512 grm. of silver $= 2.0083$ of chloride of silver. The precipitate weighed 2.033 grms. The difference of the two numbers multiplied by 1.796 , gives 0.0443612 grm. of bromine, or 0.662 per cent.

When bromides are distilled with muriatic acid and oxide of manganese, all the bromine goes over first; the moment at which the last trace of the bromine passes may be exactly recognized, as the tube exhibits a yellow coloration and a colourless part close together. It does not follow from this that no chlorine or muriatic acid has gone over when all the bromine has passed. I passed the bromine into an excess of ammonia, in which bromide of ammonium was formed. This was acidulated with nitric acid, and tested with the normal solution of silver. The precipitate was of a citron-yellow colour, and consisted of nearly pure bromide of silver, the weight of which was determined.

200 cub. centims. of the same mother-liquor $= 267.9$ grms., were distilled with muriatic acid and oxide of manganese into ammonia; this was acidulated with nitric acid, and diluted to 1 litre. 100 cub. centims. of this solution, precipitated by the silver solution, required 36.4 cub. centims. of the latter. As every cubic centimetre of the silver solution $= 0.01434$ grm. of chloride of silver, the 36.4 cub. centims. $= 0.52218$ grm. of chloride of silver. This number, deducted from 0.625 grm., leaves 0.10282 grm., and this multiplied by 1.796 gives 0.18466472 grm. as the tenth part of the amount of bromine in the whole litre; this therefore contains 1.8466472 grm. of bromine in 267.9 grms. of mother-liquor $= 0.689$ per cent.

We have thus, by three quite different methods, and with very

unequal quantities, obtained the following per-centage amounts of bromine,—0·647, 0·662, and 0·689; an agreement which may be regarded as satisfactory in the indirect analysis of a body so difficult of determination as bromine.

Regarding the last method of analysis by the evolution of the bromine, we have some remarks to make. The mother-liquor was heated to boiling by the spirit-lamp in a flask, and the fumes were conducted through a doubly bent tube into a Woulf's bottle, which contained some strong ammonia. In this, thick white vapours were formed, which at first kept at the bottom, but afterwards filled the whole bottle. From this, the excess of fumes passed into a second narrow-necked bottle, which contained water with a little ammonia. In this they settled to the bottom, and when the boiling was not too violent, they never attained any considerable height. The two bottles may always be selected of such a size that none of the fumes can escape. As soon as all the bromine is evolved, which may be distinctly seen by the colour of the empty part of the flask and the tubes, the cork of the flask is loosened a little, so that none of the bromide of ammonium may be drawn back, which would again form bromine on coming in contact with the chlorine in the tubes. The apparatus is then allowed to cool, and the contents of the two flasks and those of the tubes are poured into a graduated flask capable of containing 300 to 1000 cub. centims. It is then slightly acidulated with nitric acid, filled up to the mark with distilled water, corked, and shaken so as to mix the contents completely. 50 or 100 cub. centims. are then taken out with the pipette, put into a clean bottle, and tested with the silver solution. This is put into a burette divided into cubic centimetres and tenths, and furnished with a stopcock.

Chloride of silver cakes together into flakes; bromide of silver also does this, but to a less extent; iodide of silver, on the contrary, remains pulverulent, and is not suited for volumetric determination. The precipitates must be shaded from the light as much as possible, as exposure sets free chlorine and bromine, and thus causes the employment of too great a quantity of silver. As the distillate always contains some chlorine, but the bromine is contained in the first precipitate, it is advisable to stop the precipitation, even when a slight turbidity is still produced. The whole amount of silver is then found in the precipitate, the weight of which is determined. The washing of the precipitate is effected with the greatest certainty without filtration, first in the precipitating glass, and then in a porcelain crucible. For this purpose I always employed a siphon with a stopcock.

I wished to find a body which would set free bromine but not iodine, but I have not yet been able to discover any such body. Perchloride of iron does not separate bromine, but forms a bromide of iron, which is capable of sublimation. Bichromate of potash produces an evolution of chlorine, which passes over with the bromine.—Liebig's *Annalen*, xciii. p. 76.

PATENT.

Patent granted to J. Swindells and W. Nicholson, for Improvements in obtaining Oxygen Gas, and applying it in the Manufacture of various Acids and Chlorine, for oxidating Metallic Solutions, and for ageing and raising various colouring Matters.

THIS invention consists, first, in a method of obtaining oxygen gas, whereby it may be produced with sufficient economy for manufacturing and other purposes, in which considerable quantities are required. Secondly, in the application of oxygen gas produced by artificial means, either alone or mixed with atmospheric air, to the purposes of producing certain chemical compounds, and also for ageing and raising colouring matters employed in dyeing and printing.

The substances produced by this part of the invention are, oxalic acid, acetic acid, nitric acid, and chlorine, sulphuric acid, and highly-oxidized solutions of metals.

The method of producing oxygen gas is as follows:—Into a number of earthenware retorts, or of iron lined with earthenware, fixed in a furnace similar to retorts for producing coal-gas, and connected with a gasometer to receive the gas as it is produced, a quantity of barytes, commonly called protoxide of barium, is introduced, either alone or mixed with as much powdered silica, lime, magnesia, or alumina, or silicate of alumina, or a mixture of all or any of these substances, in order to keep the barytes from acting on the retorts, and also to keep the barytes in an open or porous state, to prevent it from fusing. It is preferred to operate on a mixture of barytes with all or any of these substances, so that the barytes amount to at least 50 per cent. of the mixture. As much of the barytes, or the barium mixture, is put into the retorts as will cover the bottom thereof about 2 or 3 inches deep, and a stream of atmospheric air is passed over the same, the mixture being kept at a dull red heat. Both hot and cold air is used, as the temperature may require. If the retorts become too hot by passing the heated air through them, then cold air is employed, and the temperature is so regulated until the protoxide of barium is converted into the deutoxide, commonly called the peroxide of barium. When this has been effected, communication is opened with the gasometer, and the temperature of the retorts is raised by increasing the firing; at the same time a moderate quantity of steam, either at a low or elevated temperature, is passed into the retort, until the oxygen gas, and some small quantity of carbonic acid gas arising from the use of common air, together with vapour of water, passes into the gasometer; the steam is condensed into water, and the carbonic acid present is removed by lime added to the water in the gasometer.

The second part of the invention is conducted as follows:—To produce oxalic acid, nitric acid and saccharine or starchy matters are used, according to the usual and well-known practice; but streams of oxygen gas, either pure or mixed with a portion of atmospheric air, are passed through the mixture of nitric acid and other matter, and so by conversion of the nitric oxide evolved, the nitric

acid is continually reproduced, until the operation is complete; or the oxygen gas is passed along with the compounds of nitrogen and oxygen produced in the manufacture of oxalic acid as usually conducted, and by its agency the nitric acid so employed in the manufacture is recovered. In manufacturing acetic acid, or common vinegar, the patentees apply oxygen gas, either pure or mixed with atmospheric air, to any fermented saccharine solution, by passing streams thereof through the solution according to any known methods now employed for passing atmospheric air in the speedy production of vinegar. In producing nitric or nitrous acid, nitrogen, or any gaseous matter containing the same, is passed, in conjunction with oxygen gas, in their atomic proportions, or, in preference, with an excess of oxygen, through earthenware pipes heated to full redness, and filled with any porous substance that will stand the heat and action of the acid vapour produced. By this process deutoxide of nitrogen is produced, which is converted into nitric acid by being brought into contact with oxygen gas and the vapour of water. To manufacture chlorine, oxygen gas, either pure or mixed with atmospheric air, is passed through the chloride of manganese or iron at a red heat; the products are peroxides of the metals and chlorine gas. In producing chlorine from hydrochloric acid, to any given quantity of this acid one-half its weight of common nitric acid is added, and the same is heated so as to produce chlorine and nitrochloric acid, which is brought into contact with oxygen gas, either in the same vessel or in an intermediate one, with the vapour of water; when the nitrochloric acid or compound of nitrous and hydrochloric acids are decomposed, any nitrous gas is converted into nitric acid for renewed operations, and the chlorine gas evolved is conveyed away by pipes for its intended use; or chlorine gas may be produced by passing oxygen gas into mixtures or solutions of hydrochloric acid, and the oxides of manganese and iron in a liquid state, or by passing the same through heated earthenware tubes; but the two first processes are preferred. The patentees produce sulphuric acid by passing sulphurous acid gas with oxygen gas, either pure or mixed with atmospheric air and the vapour of water, through red-hot earthenware pipes filled with any porous substance that will stand acid action, and condense the acid so produced in any convenient lead or earthenware apparatus, adding the vapour of water if required. In producing highly-oxidized solutions of various metals, as the persulphate of iron for instance, oxygen gas is passed through the solution by any of the commonly practised methods, and it is peroxidized either with the conjunction of nitric acid or without the same. Oxygen gas, either pure or mixed with common air, is also used to age or peroxidize the mordants made use of in printing or dyeing textile materials or fabrics. It is also employed, either pure or mixed with atmospheric air, for "raising" the colours employed for dyeing or printing, either during the process of manufacturing such colours, or after they are applied to the fabrics—in the latter case, by passing the goods through a vessel or room into which the gas is admitted.—Dated October 14th, 1852.

THE CHEMICAL GAZETTE.

No. CCC.—April 16, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Caprylic Aldehyde. By Dr. LIMPRICHT.

SOME years since, Bouis stated*, that when ricinoleic acid is distilled with hydrate of potash, caprylic or cœnanthylic alcohol is formed. Later investigations have left it undecided which of the two alcohols are obtained in this way. Moschnin, Cahours, and Bouis stated that they obtained the former, Wills and Railton the latter.

According to my observations, the distillation of various kinds of castor oil, or the soaps prepared from them with hydrate of potash, furnishes neither caprylic nor cœnanthylic alcohol, but caprylic aldehyde.

The greater part of the fluid obtained by this operation could be brought by distillation to a constant boiling-point of $351^{\circ}6$ F.; it was colourless, possessed a pleasant aromatic odour, a specific gravity of 0.820, and the general physical properties described by other chemists.

A ready means of recognizing the aldehydes and acetones is afforded by their power of forming crystallizable compounds with the alkaline bisulphites; no known alcohol exhibits a similar property. If the so-called caprylic or cœnanthylic alcohol be shaken with a concentrated solution of bisulphite of potash or soda, the whole fluid soon solidifies from the separation of a quantity of crystals of sulphite of caprylaldehyde and potash or soda.

The formation of these crystals takes place so readily, that it furnishes the most advantageous method of separating the caprylic aldehyde from the crude products of distillation. The crystalline jelly obtained is pressed between frequently-changed papers, washed with cold alcohol, and dried over sulphuric acid; after solution in hot water, pure caprylic aldehyde separates, which is deprived of water by chloride of calcium, and may be rectified with an immersed thermometer.

These compounds of caprylic aldehyde cannot be purified by recrystallization; they also continually give off sulphurous acid, although only in small quantity. It was consequently to be expected that analysis would not give correct numbers for the proportion of the caprylic aldehyde to the alkaline bisulphite. The decomposition does not however extend to the organic substance which

* Chem. Gaz., vol. xii. p. 228.

they contain ; and the proportion of the carbon to the hydrogen and oxygen, which was ascertained by combustion, furnishes the proof of the assertion made above.

Sulphite of caprylic aldehyde and potash, $\left. \begin{matrix} \text{C}^{16}\text{H}^{15}\text{O}^2 \\ \text{K} \end{matrix} \right\} \text{S}^2\text{O}^4 + 3\text{Aq.}$

—The potash was first determined by calcination, and then converted into sulphate by treatment with sulphuric acid, and weighed in this form. The sulphurous acid was converted into sulphuric acid by muriatic acid and chlorate of potash, and this precipitated by chloride of barium. The combustion was effected with chromate of lead and oxygen gas. Analysis gave :—

	Calculated.		Found.			Average.
KO	47	18·3	20·17	20·04	..	20·1
2SO ² ..	64	24·9	26·6	26·7	26·5	26·6
C ¹⁶	96	37·8	35·16	..	..	35·16
H ¹⁸	18	7·0	6·67	..	..	6·67
O ⁴	32	12·0	..	..	..	11·47

From the comparison of the ascertained numbers with those obtained by calculation, it appears that the compound with bisulphite of potash was impure, and that the latter had lost sulphurous acid by evaporation, for the ascertained amount of potash, 20·1, should have furnished 27·3 of sulphurous acid. Nevertheless the numbers obtained by the combustion agree with the composition of caprylic aldehyde ; thus if the ascertained amount of potash and sulphurous acid, 46·7, be deducted from 100, there remains 53·3 for the caprylic aldehyde and 2 atoms of water ; and if the carbon, hydrogen, and oxygen given by the combustion for these 53·3 parts be extended to 100, we get,—

Caprylic aldehyde+2 at. Aq.		Found.	Caprylic alcohol+2 at. Aq.	
C ¹⁶ H ¹⁸ O ⁴ .			C ¹⁶ H ²⁰ O ⁴ .	
C ¹⁶	65·7	65·9		64·8
H ¹⁸	12·3	12·5		13·5
O ⁴	22·0	21·5		21·7

As these compounds of caprylic aldehyde cannot be recrystallized, I was induced to analyse the caprylic aldehyde itself.

The caprylic aldehyde employed for this purpose was rectified immediately before the analysis, and only that portion which possessed a constant boiling-point of 351°·6 F. was employed. The combustion was effected with granular oxide of copper, and the reduced copper again oxidized by dry oxygen gas. Analyses :—

	I.	II.	III.	IV.
C	74·45	..	74·7	74·8
H	12·43	12·43	13·1	13·1

These numbers agree with the composition of caprylic aldehyde, but not with that of caprylic alcohol :—

Caprylic aldehyde,		Caprylic alcohol,	
C ¹⁶ H ¹⁶ O ² .		C ¹⁶ H ¹⁸ O ² .	
C ¹⁶	75·0	C ¹⁶	73·84
H ¹⁶	12·5	H ¹⁸	13·84
O ²	12·5	O ²	12·32

Caprylic aldehyde becomes acid in the air, like the other aldehydes; Railton, who took it for *œnanthylic* alcohol, passed oxygen gas through it whilst boiling, and in this manner obtained a large quantity of acid.

If the body in question were really caprylic alcohol, the true aldehyde must be obtainable from it by oxidizing substances. When it was distilled with a solution of chromate of potash and sulphuric acid, a part of it was converted into acid; but the greater portion was unchanged, for this product, which was purified by the preparation of the compound with bisulphite of potash, furnished on analysis 74.49 per cent. of carbon and 12.67 per cent. of hydrogen.

The facts here stated appear to me to prove sufficiently that caprylic aldehyde is produced by the treatment of ricinoleic acid with fusing hydrate of potash. The analyses and experiments made by the above-mentioned chemists, on the other hand, speak strongly in favour of the alcoholic nature of this product.

Our knowledge of the aldehydes belonging to the series of fatty acids, especially of those with a high atomic weight, is still too limited to enable us to get rid of this contradiction. It appears to me that the best way to arrive at decided results, will be to submit caprylic aldehyde and the nearly-allied substance *œnanthole* to a comparative investigation.—Liebig's *Annalen*, xciii. p. 242.

On Salicylic Acid. By R. PIRIA.

Salicylic acid is considered to present a remarkable exception amongst monobasic acids, that it forms acid *æthers*, which are rather comparable with the acid *æthers* of the polybasic acids than with the neutral *æthers*. The author has found that this supposed peculiarity does not exist, and that salicylic acid, which has hitherto been regarded as monobasic, is in reality a very well characterized bibasic acid, and forms salts with 2 equivs. of base so readily, that it is singular that these should have remained so long unnoticed. He denominates the previously known salts with 1 equiv. of base *acid salicylates*, and gives the name of *neutral salicylates* to the new salts, with 2 equivs. of base, discovered by himself.

Neutral Salicylate of Baryta is prepared by adding a concentrated solution of hydrate of baryta to a boiling concentrated solution of the acid salt; the neutral salt, which is far less soluble than the acid salt, separates immediately in the form of small, white, laminar crystals, which are purified by recrystallization from boiling water. This salt possesses a very distinct alkaline reaction; its watery solution is decomposed by carbonic acid, acid salicylate of baryta remaining in solution, whilst half the base is thrown down in the form of carbonate. The composition of the neutral salt is $C^{14} H^4 Ba^2 O^6 + 4 Aq$; at 212° F. it loses the 4 equivs. of water, and becomes anhydrous.

Neutral Salicylate of Lime is prepared with equal ease by adding a solution of lime in sugar to a solution of acid salicylate of lime; the neutral salt separates immediately in the form of a nearly inso-

luble sandy precipitate, which possesses an alkaline reaction and is decomposed by carbonic acid, like the baryta-salt. The composition of the neutral lime-salt is $C^{14} H^4 Ca^2 O^6 + 2Aq$.

The *Neutral Lead-salt* is anhydrous, and forms a heavy, white, crystalline powder, of the composition $C^{14} H^4 Pb^2 O^6$. It is easily obtained by the addition of tribasic acetate of lead to a boiling saturated solution of acid salicylate of lead. If this acid lead-salt be decomposed by a slight excess of ammonia, and the mixture be boiled, a pentabasic salicylate of the formula $C^{14} H^4 Pb^2 O^6 + 3PbO$ is thrown down in the form of an insoluble, light, white powder, composed of microscopic pearly laminæ.

The compounds of salicylic acid with oxide of copper have not been investigated. The author prepared the acid salicylate of copper by decomposing acid salicylate of baryta with a solution of sulphate of copper. The fluid separated from the sulphate of baryta contained the acid salicylate of copper. This salt crystallizes in long greenish-blue needles, of the composition $C^{14} H^3 CuO^6 + 4Aq$, which lose their water of crystallization far below $212^\circ F$. This salt, when heated in a small quantity of water insufficient for its solution, melts below $212^\circ F$., and becomes converted into a neutral salt, which remains undissolved; the water contains free salicylic acid. The salt is similarly decomposed by æther in the cold.

The neutral salicylate of copper thus obtained is a light, nearly insoluble powder, of a yellowish-green colour; its composition is $C^{14} H^4 Cu^2 O^6 + 2Aq$.

The author has also obtained two other neutral salicylates, in which the 2 equivs. of base are two different oxides, namely, a salicylate of copper and potash, $C^{14} H^4 KCuO^6 + 4Aq$, crystallizing in beautiful emerald-green laminæ, and a salicylate of copper and baryta, $C^{14} H^4 BaCuO^6$, which forms a crystalline powder.—Liebig's *Annalen*, xciii. p. 262.

On a new mode of Formation of Amarine and Lophine.

By Dr. A. GÖSSMANN.

In a recent paper on the preparation of æthylamine from bisulphite of aldehyde-ammonia by distillation with lime, the author expressed the opinion that the analogous compounds of the other aldehydes would probably behave in the same manner, and give origin to the corresponding bases. He first experimented upon the oil of bitter almonds, the aldehyde of benzoic acid. The sulphite was prepared by mixing a concentrated alcoholic solution of bisulphite of ammonia with a sufficient quantity of oil of bitter almonds, and collecting the mass of crystals, when it ceased increasing in quantity. This, when perfectly dry, was mixed with from three to four times its volume of very dry freshly-prepared hydrate of lime; the mixture was put into a large retort, and covered with a thin stratum of lime; a well-cooled receiver was then attached to the retort, and the latter quickly surrounded with coals as far as it was full, and heated to about 350° – $392^\circ F$. The cool part of the neck

of the retort was immediately covered with a white apparently amorphous mass, which as the heat reached it flowed in oily drops into the receiver. This substance is amarine. The heat was maintained as long as oily streaks appeared in the neck of the retort, and the sublimate increased in its hottest part. The process was carried on as described in the author's former paper.

The amarine is found partly in the receiver, suspended in an ammoniacal fluid, which is rendered turbid by a small quantity of oil of bitter almonds, and partly in the lower part of the neck of the retort; the upper part of the neck always contains a larger or smaller quantity of another substance, partly in the form of tufts of acicular crystals, and partly in radiating masses spreading over the glass. This second substance is *lophine*.

To collect the amarine and free it from a small quantity of oleaginous products, it is washed with a little cold alcohol in a receiver, dissolved by the addition of alcohol and muriatic acid, and precipitated by ammonia. It is purified by recrystallization and treatment with animal charcoal. The analysis of the muriate gave,—

	Calculated.	Found.
C ⁴²	75.33	75.15
H ¹⁹	5.68	5.62
N ²	8.37	
Cl	10.61	

0.4045 grm. of chloride of platinum and amarine gave on calcination 0.0805, or 19.8 per cent. of platinum. The formula C⁴² H¹⁹ N² Cl + PtCl₃ requires 19.58 of platinum.

The lophine found in the retort and in the upper part of the neck was dissolved in hot alcohol, and crystallized after treatment with animal charcoal. It was generally so pure, that after a single crystallization it formed dazzling white needles; it fused at 409° F., volatilized at that temperature without change, and solidified on cooling into a beautiful radiating mass. The analysis of the pure base, after repeated crystallization from alcohol, gave the following numbers:—

	Calculated.	Found.
C ⁴⁶	85.98	85.69
H ¹⁷	5.30	5.5
N ²	8.72	

0.3205 grm. of chloride of platinum and lophine furnished 0.0605, or 18.89 per cent. of platinum. The formula C⁴⁶ H¹⁶ N² Cl + PtCl₃ requires 18.72 per cent.

The formation of lophine only commences when the retort has reached a very high temperature, and may be satisfactorily explained by the fact, that the amarine formed in the interior of the mass can only escape gradually, and that part of it only escapes when the temperature of the exterior produces its decomposition. The formation of lophine is consequently much assisted by employing a large retort, heating it rapidly and strongly, and covering its upper part with a few coals, so as to fulfil as quickly as possible all the condi-

tions necessary to make the amarine pass through a strongly heated space. In this manner the author has obtained crystals of lophine of an inch in length, even when operating with small quantities.

It appears to be unnecessary to employ the crystallized compound of the aldehyde; all that is required is to mix a very concentrated solution of bisulphite of ammonia with the corresponding quantity of oil of bitter almonds, dissolved in a little alcohol, and to evaporate the mixture as quickly as possible to dryness on the water-bath. The mass thus obtained is mixed with freshly-prepared and perfectly dry hydrate of lime, as, if either of these ingredients be too moist, a great part of the compound is decomposed at the commencement of the distillation, forming ammonia and oil of bitter almonds. As however in this mode of treatment a little benzoic acid is always formed in the mass, a quantity of benzole corresponding with that of the benzoic acid is always observed in the distillate. The removal of this is not very difficult, as it is quickly volatilized by heating the product of distillation to 176° or 194° F.—Liebig's *Annalen*, xciii. p. 329.

On the Anilide Compounds of Tartaric Acid. By A. E. ARPPE.

In a previous memoir on the anilide compounds of pyrotartaric acid, the author has pointed out that when pyrotartaronitrile is treated with fixed alkalies, a basic substance is separated, which has the composition of nitraniline.

Tartaric acid forms a crystallizable salt with aniline, which, if tartaric acid be regarded as a monobasic acid, is the bitartrate. This salt cannot be heated much over 212° F. without decomposition; if it be kept for some time between 266° and 284° F., it becomes brown, with formation of vapours of aniline and water, and a new crystalline body, which is distributed throughout the whole mass, is produced. At 302° F. partial fusion occurs, and it soon becomes impossible to detect unchanged aniline by a solution of chloride of lime.

The mass obtained is boiled with water, by which the *tartanilide* is extracted; this is purified by repeated crystallization and treatment with animal charcoal.

The brown mass which remains undissolved in the water is boiled with strong alcohol, which dissolves it completely. On cooling, fine crystals separate, which may be obtained perfectly colourless by the usual methods. These are *tartanilide*.

Tartanilide is insoluble in water, difficult of solution in æther, and does not dissolve in any great quantity even in boiling alcohol. It separates from its saturated alcoholic solution on cooling in fine colourless needles, which, when collected on a filter and pressed, become melted together into pearly laminar masses, which retain their cohesion when dried. It may be heated to 482° F. without decomposition; it decomposes when fused, but sublimes unchanged a little below its melting-point; and when carefully heated between two watch-glasses, furnishes a sublimate of shining laminæ with a

beautiful play of colour, which however, in consequence of the difficulty with which they are volatilized, attach themselves to the portion remaining unmelted. At a higher temperature, a lustreless, crystalline, or mealy sublimate is obtained.

Tartanilide is a very stable substance; it may be boiled in alkaline solutions without undergoing any change; it is dissolved with difficulty by hot muriatic acid, by nitric acid with partial decomposition; sulphuric acid alone dissolves it easily.

The analysis gave 63·61 per cent. of carbon and 5·40 per cent. of hydrogen. The compound $C^{32}H^{16}N^2O^8 = 2(C^{12}H^7N)C^8H^6O^{12} - 4HO$ has the following theoretical composition:—

C^{32}		192	64·000
H^{16}		16	5·334
N^2		28	9·334
O^8		64	21·332

Tartanile is dissolved very readily by water and alcohol. It separates from its hot concentrated solutions either as a lustreless, white, finely granular powder, or in pearly laminæ. Slow cooling and perfect purity are favourable to the formation of the crystallized modification, whilst sudden cooling and the presence of a little tartaric acid appear to produce the granular form.

Tartanile bears a heat of above $392^{\circ}F$. without decomposition, but at this temperature the granular variety passes into the crystalline form without any chemical change; the sublimate produced forms an extremely fine woolly crystallization of unaltered tartanile. At $446^{\circ}F$. fusion and decomposition take place.

It has no taste, but reddens litmus-paper distinctly even when quite pure. It dissolves with some difficulty in æther, but is readily taken up by other solvents. Its analysis gave 57·71 per cent. of carbon, and 4·38 per cent. of hydrogen. The formula of tartanile, $C^{20}H^9NO^8 = C^{12}H^7N, C^8H^6O^{12} - 4HO$, gives the following composition:—

C^{20}		120	57·97
H^9		9	4·35
N		14	6·76
O^8		64	30·92

Tartanilic Acid is obtained by boiling tartanile for about a quarter of an hour with a solution of ammonia, evaporating the excess of ammonia by a gentle heat, adding an excess of baryta-water to the solution and decomposing the precipitate produced, after washing it, with sulphuric acid. From the filtered solution tartanilic acid separates partly in pale red wart-like masses of crystals, and partly in shining laminæ. When purified with animal charcoal, it forms very lustrous colourless laminæ. It fuses at $356^{\circ}F$., becoming partially decomposed with loss of water; it dissolves readily in water and alcohol, but much less so in æther.

Tartanilate of Ammonia, when evaporated over sulphuric acid, furnishes a very soluble and efflorescent crystalline mass. A solution of this salt gives no precipitate with lime-water even after the

addition of ammonia; but if potash be added, a turbidity is produced, which increases by boiling, and becomes converted into an abundant voluminous precipitate; chlorides of calcium and barium give no precipitate even in the presence of an excess of ammonia; baryta-water produces a copious precipitate, which is soluble in muriate of ammonia, and chloride of iron causes a yellow precipitate.

Tartanilate of Baryta is very soluble in boiling water, and when evaporated shoots into shining irregular spangles. 0.1458 grm. left 0.049 of carbonate of baryta = 26.10 per cent. of baryta. The compound $\text{BaO}, \text{C}^{20} \text{H}^{10} \text{NO}^9$ requires 26.15 of baryta ($\text{Ba} = 68.5$).

Tartanilate of Silver forms a white, somewhat soluble powder. It furnished 32.66 per cent. of silver; the formula $\text{AgO}, \text{C}^{20} \text{H}^{10} \text{NO}^9$ requires 32.55 per cent.

From these analyses of the baryta and silver salts, the author considers that it is sufficiently proved that the formula of tartanilic acid is $\text{C}^{20} \text{H}^{11} \text{NO}^{10}$; he did not analyse the acid.

On the action of Nitric Acid upon Tartanile and Tartanilide.—Nitric acid, rectified with sulphuric acid, acts violently upon these bodies. On mixing them with the acid, a considerable elevation of temperature takes place, which is accompanied by the formation of picric acid. If however this heating is avoided by surrounding the vessel with snow, and adding the anilide compounds in small quantities, a solution is obtained, from which water separates a yellowish body; this is perfectly insoluble in water, extremely difficult of solution in alcohol, and appears as a crystalline powder under the microscope.

If this nitro-compound be boiled with carbonate of soda, a portion of it is dissolved, but no crystals separate from the solution. The greater part remains undissolved, and appears to contain picric acid.

The author adds that the *anilide compounds of racemic acid* appear to be identical with those of tartaric acid, as he has prepared compounds from racemate of aniline, which did not differ in their external characters from tartanile and tartanilide.—Liebig's *Annalen*, xciii. p. 352.

On the Action of Air upon Alkaline Arsenites.

By Dr. R. FRESSENIUS.

The author found that solution of arsenite of soda, intended for volumetric analyses, was subject to alteration when in contact with air; it takes up a portion of oxygen, and becomes gradually converted into arseniate of soda.

In testing two portions of the same solution of chloride of lime with a freshly-prepared solution, and one that had been long kept in a half-filled bottle, he found that a great deal more of the latter was required to produce the desired reaction; and the addition of solution of nitrate of silver produced the usual pale yellow precipitate of arsenite of silver in the freshly-prepared solution, whilst the old one furnished a precipitate with a strong tinge of reddish-brown.

To follow the subject further, he prepared a solution of arsenite

of soda, and put it into three bottles, one of which was completely filled, another about one-sixteenth, and a third about one-eighth full. The two former were well closed with glass stoppers, the third was left open, and the stopper of the second was removed from time to time. In three weeks the contents of the bottle, which had remained closed, were found unchanged, whilst those of the other two bottles were almost entirely converted into solutions of arseniate of soda, which gave a brownish-red precipitate with nitrate of silver.

This renders it important that chloride of lime manufacturers, and others who use the solution of this salt, should preserve it carefully from the air; and the author recommends that the quantity necessary for a month's consumption should be prepared, and put into thirty well-stopped bottles, each of which should be sufficient for one day. The fact is also of importance in medicine, as the form in which arsenic is most commonly used is that of solution of arsenite of potash (*solutio arsenicalis Fowleri*), and that salt may absorb oxygen as readily as the arsenite of soda. In fact, the author found, by testing the solution obtained from an apothecary, that it contained a considerable quantity of arseniate of potash.—Liebig's *Annalen*, xciii. p. 384.

On the Sublimation of Naphthaline. By J. OTTO.

The author recommends the following process for the preparation of pure colourless naphthaline from the crude brown product contaminated with oil:—

About half a pound of crude naphthaline is put into a large porcelain dish, covered closely with a piece of blotting-paper, and placed in the sand-bath. In the course of a few hours the whole dish is found filled with most beautiful dazzling white laminæ of naphthaline. When the saucer has cooled, these are removed, and the sublimation may be recommenced. It is advisable to cover the cake of naphthaline at the bottom of the dish with a few pieces of blotting-paper, which suck up the oil. The last sublimate is yellowish.—Liebig's *Annalen*, xciii. p. 383.

ANALYTICAL CHEMISTRY.

On the Chemical Detection of Blood-stains. By H. ZOLLIKOFER.

It might appear that by the employment of the microscope, which *in itself* is perhaps the most delicate test for blood, chemistry would be entirely thrown into the background; but this instrument, as also unfortunately all the chemical methods for the detection of blood hitherto published, are either of limited application or in many

cases quite inapplicable. The microscope will still probably remain the most certain and delicate indicator of fresh blood or blood dried by itself; but when it is necessary to recognize blood which has dried upon and with other bodies, such as iron rust, earth, &c., it is generally impossible to procure the blood-corpuscles in such a form that we can venture to give an opinion as to their presence.

All those chemical methods which do nothing more than indicate the presence of albumen, the common constituent of many organic fluids, are inadmissible, as is also, it appears to me, the *cyanogen test* very recently recommended by Löwe*, which certainly proves nothing but the presence of nitrogen in the suspected substance. That a chemist should testify to the presence of blood because *alcoholic sulphuric acid* gave an extract of a more or less red colour, which on evaporation and incineration left a residue containing oxide of iron, is only to be admitted if the object under examination contains no iron but that of the hæmatine; so that this process cannot be employed in many cases, especially in the examination of a suspicious iron rust.

The following method is founded upon that lately described by H. Rose†. It was adopted in a case in which it was necessary to determine whether certain reddish-brown spots upon hatchets, wearing apparel, earth, &c., were produced by blood; and the object in view was, of course, to obtain a method which should as far as possible apply to all objects, and which should furnish reliable results by means of a few decisive reactions.

Regard was had principally to two constituents of blood, albumen and hæmatine, and especially to the latter, which indeed is so characteristic of blood, that its presence alone is sufficient to enable us to conclude that blood is present. By the introduction of a better reaction for hæmatine than that proposed by Rose, it appears to me that his method, which is the only serviceable one hitherto proposed, is rendered capable of more general application.

The following is the description of the method followed in the examination of blood-stained iron rust; in the first series (A) it is supposed that the blood has only been in contact with the iron for a short time, *i. e.* not for several months; the latter case is described under B.

A. The iron rust is carefully scraped off the metal with a knife, and digested for a considerable time in a porcelain cup with a moderate quantity of water not at a higher temperature than 122° F.; the solution obtained is filtered. This contains the albumen, the soluble salts of the blood and the hæmatine; the latter, if the solution be not too much diluted, communicates a reddish colour to the water, even when its quantity is but small.

This solution is now heated to boiling, which produces either a dingy reddish clot or a mere opalization, according to the quantity of albumen and hæmatine. It is as well to neutralize the slightly

* See Chem. Gaz., vol. xii. p. 233.

† Casper's Vierteljahrssch. für Gerichtl. Med., iv.

alkaline fluid by a little diluted acetic acid. These flakes are then dissolved in hot solution of caustic potash, when the hæmatine causes the fluid, when not too much diluted, to appear green by transmitted, red by reflected light. This experiment is best performed in a white test-glass. To this, or a portion of the original watery solution, an excess of concentrated solution of chlorine is added; when the fluid is shaken, white flakes of precipitated albumen and chloride of hæmatine separate, and collect at the surface especially.

When the material is sufficient, H. Rose tests it for albumen with nitric acid and tincture of galls.

Of the reactions just described, the second alone indicates the presence of hæmatine. But the dichroism of the alkaline solution of hæmatine may be wanting when the solution is much diluted, although a distinct deposit may be produced by solution of chlorine. From this reaction alone however it would not be safe to decide on the presence of blood, as the precipitate may arise from albumen as well as from chloride of hæmatine, or from both these substances; and it is evidently useless to attempt the separation of the chloride of hæmatine by solution in alcohol, when operating upon such small quantities.

Hæmatine is the only organic body into the composition of which iron enters; according to Mulder's formula it is $C^{41} H^{92} N^3 O^6 Fe$. By the action of chlorine upon hæmatine, suspended or dissolved in water, white chloride of hæmatine, *free from iron*, is separated in flakes, whilst the iron remains in solution in the form of chloride. The most sensitive reagent for peroxide of iron is perhaps sulphocyanide of potassium; and I found that by means of that reagent the presence in the filtrate of the iron separated from the hæmatine by chlorine may be easily proved; and this test is so delicate, that when a small old blood-spot was carefully washed with a little water, solution of chlorine produced an unmistakeable reaction, in the form of a whitish turbidity, which did not form a sediment until the lapse of several hours, and the addition of sulphocyanide of potassium to the clear filtrate produced a distinct reddish-yellow colour, which was particularly evident on looking down into the fluid in the test-glass.

B. In this case we suppose the iron rust and blood to have been long in contact. According to H. Rose, hæmatine possesses the property of combining in time with hydrated oxide of iron (iron rust), and thus becoming insoluble in water. This combination must therefore be destroyed, which is best effected by boiling the rust with dilute solution of caustic potash, by which the hæmatine is taken up. Too great an excess of potash must however be avoided, as this impedes the supersaturation with solution of chlorine, and necessitates the formation of very dilute fluids. The solution thus obtained is treated in the same manner as under A. If the former process has given negative results, the rust should always be treated with solution of potash, to make sure that no combination has taken place between the hæmatine and the rust.

It is necessary however to ascertain that no soluble iron salts exist in the watery extract; this is done by testing the extract first of all by means of ferrid- and ferrocyanide of potassium. When such free salts of iron are present, the only way to obtain reliable results is to prepare an alkaline and a watery extract from two analogous suspected substances. The presence of albumen and hæmatine in the watery extract is determined by means of solution of chlorine; all the organic substances in the alkaline extract, which contains no such salts, may be separated by solution of chlorine, and the iron of the hæmatine determined as above. The two reactions together may be regarded as proof.

G. Rose has shown that certain non-volatile organic substances prevent the precipitation of oxide of iron by alkalies, and even render it very soluble. The question therefore arises, whether alkaline fluids, when employed in the extraction of mixtures of substances containing albumen and hæmatine with oxide of iron at a boiling heat, may not possess the power of dissolving oxide of iron, thus giving indications of iron which do not arise from hæmatine. Experiments made with white of egg, the prototype of the albuminous fluids, showed that this at any rate possesses no such property.

This method may be applied with very little modification in the examination of traces of blood upon clothing, wood and earth. Suspected *wearing-apparel* (of linen, cotton, wool or silk) is cut up, and extracted by long treatment with cold or luke-warm water. The subsequent treatment is as already described. For the recognition of blood upon *wood-shavings*, the best method is that of H. Rose, who attaches the piece of wood to a linen thread, and suspends it in water in a test-glass, sinking it by means of a weight. In a little time, if blood be present, reddish streaks fall towards the bottom of the glass, whilst a voluminous flocculent mass remains upon the wood. This may be recognized as fibrine under the microscope, and uninjured blood-corpuscles may generally be distinguished in it. The reddish fluid may then be easily tested by the above method.

According to H. Rose, hydrate of alumina also possesses the property of combining with hæmatine to form an insoluble compound, although in a less degree than oxide of iron. In the examination of such substances, if it be supposed that the blood has long been in contact with the earth, the objects must be boiled with solution of caustic potash, either at first or after extraction with water; the alkaline extract is of a dark brown colour, in consequence of the presence of dissolved humus. Supersaturation of the fluid with acids produces brown gelatinous precipitates of humous substances. To determine the hæmatine in an alkaline solution of this kind, it is supersaturated with concentrated solution of chlorine, which decolorizes the fluid, and produces separation of any proteine substances and hæmatine that may be present, whilst the humus remains in solution. The filtrate is then tested for iron with sulphocyanide of potassium.—Liebig's *Annalen*, xciii. p. 247.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On a new Process for Electro-gilding. By M. BRIANT.

A MODIFIED process for this purpose has been proposed by a M. Briant, and has been the subject of a favourable report, made by M. Jacobi to the Academy of Sciences at St. Petersburg. It consists essentially in the substitution of the oxide for the chloride of gold in the preparation of the gilding-bath, and in the employment of a very feeble current from a constant or sustaining battery.

52 grms. (=802·88 grs.) of gold are to be dissolved in nitromuriatic acid, and the solution evaporated, for the purpose of obtaining the chloride of gold dry, and as free as possible from acid. This chloride is then dissolved in 5 kilogrms. (=11 lbs.) of hot water, and 100 grms. (1544 grs.) of well-sifted magnesia added, and allowed to digest at a moderate temperature. The oxide of gold which is separated is found in combination with the magnesia. The magnesia, well washed, is then treated with water acidulated with nitric acid, in the proportion of 375 grms. of acid to 5 kilogrms. of water. The magnesia is dissolved by the acid, leaving the simple hydrated oxide of gold, which is now thrown upon a filter and washed until it is quite free from acid.

It is with the oxide of gold, thus prepared, that M. Briant proposes to form his bath. He takes of—

Yellow prussiate of potash	500 grms.
Caustic potash	120 grms.
Water	5 kilogrms.

To this solution the oxide of gold with the filter is added, and the whole is boiled for twenty minutes. The oxide of gold dissolves, and there is formed at the same time a precipitate of sesquioxide of iron. It is allowed to cool, and is then filtered, by which a yellow liquid fit for use is obtained. The objects to be gilded should be well cleaned, and attached to the negative pole of an element of Daniell's battery, while a plate of platinum is attached to the positive pole.

The gilding may be effected either in a warm or cold solution; in the first case the deposit forms more rapidly, but with less delicacy. In order to obtain a durable deposit, analogous to fire-gilding, several hours are required. When the liquid is exhausted of its gold, fresh oxide is added, by which a further precipitation of oxide of iron is produced. The gilding obtained by this process admits of being burnished, and of undergoing all the operations employed to produce *mat* or dead gold.

One of the most difficult problems to solve in this branch of manufacture is the production of dead surfaces. Although we know the nature and manipulation of the process, it is only the Parisian workmen who perfectly succeed in this field; hence it is that these operations are always conducted by French workmen, as well in native as in foreign establishments of importance.

The production of dead gold in the ordinary way is always accompanied by loss of metal, inasmuch as it necessitates a system of corrosion of the surface by chlorine. By Briant's process a matted surface can be obtained by galvanic agency not inferior to the best of Paris, while it does not require any of the subsequent operations required in fire-gilding. The mat appearance is spontaneously produced as soon as the coating of gold has acquired a certain thickness; it is most beautiful when the operation is carried on in the cold. By a very simple artifice a more or less reddish tint on the one hand, or a whitish one on the other, is produced; it is merely requisite to dilute the bath with more or less water.

When the objects to be gilded are polished and brilliant, the electro-gilding will also be brilliant, and it requires a longer time and a thicker coating of gold to produce a deadened surface. It is therefore important to communicate, in the first instance, a deadened surface to the objects by the process employed in fire-gilding; or, more æconomically, by covering them at once with a thin pellicle of copper by the electric agency, which, as is well known, produces a beautiful matted surface. When any part of the object is to be protected from the action of the gilding process, the choice of the substance to be used in "stopping out" these parts is of importance, for it must be remembered that the bath is alkaline; for this purpose plaister impregnated with an alcoholic solution of lac is recommended.—*Bulletin de la Société d'Encouragement*.

New Composition for Types, Stereotype Plates, &c.

By H. EHRHARD.

The following composition has been patented in Bavaria:—The principal constituent is zinc, to which the requisite properties are given by the addition of tin, lead and copper. According to the purity of the metals and the loss during fusion, the proportions require to be varied a little. The following proportions are recommended:—89 to 93 parts of zinc, 3 to 6 parts of tin, 2 to 4 parts of lead, and 2 to 4 parts of copper.—*Kunst- und Gewerbeblatt. für Baiern.*, 1854, p. 671.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 8, 1855. (Sir Benjamin Brodie, Bart., Vice-President, in the Chair.)

"On Circumstances modifying the Action of Chemical Affinity."
By J. H. Gladstone, Ph.D., F.R.S.

The question intended to be solved in this communication is,—what takes place when two binary compounds AB and CD are brought together under such circumstances that both they themselves and the products of their mutual action remain free to react?

Do they, according to a generally received opinion, remain unaltered, or, should the affinities so preponderate, become simply AB and CB? Or do A and C, according to Berthollet's view, divide themselves in certain proportions between B and D, the said proportions being determined not solely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies? And, supposing the latter to be the correct view, do the amounts of AD and CB produced by the reaction, increase progressively with the relative increase of AB, or do sudden transitions occur, such as Bunsen and Debus have recently observed in certain cases where the products were removed at once from the field of action?

A reply was sought in the colours produced upon mixing different salts in aqueous solution. There were not many coloured salts suitable for the purpose, as it generally happens that a base gives the same colour with whatever acid it is combined, and *vice versâ*; but the compounds of sesquioxide of iron were peculiarly adapted to the requirements of the experiment, as some are intensely coloured while others are nearly colourless.

The circumstances that attended the formation of the blood-red sulphocyanide were first fully examined. On mixing known quantities of different ferric salts with known quantities of different sulphocyanides, it was found that the whole of the iron was never converted into the red salt; that the amount of it so converted depended on the nature both of the acid combined with the ferric oxide, and of the base combined with the sulphocyanogen; and that it mattered not how the bases and acids had been combined previous to their mixture, so long as the same quantities were brought together into solution. The effect of mass was fully tried by mixing equivalent proportions of ferric salts and sulphocyanides, and then adding known amounts of either one or the other compound. It was found that in either case the amount of red salt was increased; and that when the numbers of equivalents of the salt added were taken as abscissæ, and the amounts of red sulphocyanide produced, as ordinates, the numbers observed in the experiments gave regular curves, though not belonging to the second order. The curves representing the experiments in which sulphocyanide of potassium was mixed with ferric nitrate, chloride, or sulphate, appeared to be the same, but hydrosulphocyanic acid gave a different curve. The deepest colour was given when nitrate of iron was mixed with the sulphocyanide, but even upon the admixture of one equivalent of the former with three of the latter, only 0.194 equiv. of the intensely red ferric salt was formed, and when 375 equivalents of sulphocyanide of potassium had been added there was still a recognizable amount of nitrate of iron undecomposed. It was found that the addition of a colourless salt not only reduced the colour of a solution of ferric sulphocyanide, but also that the reduction increased in a regularly progressive ratio according to the mass of the salt.

Other ferric salts were likewise examined. The black gallate gave results precisely analogous to those obtained by means of the sulphocyanide; the red meconate also confirmed Berthollet's views,

but the action of mass was rendered obscure by the formation of double or of acid salts; the red pyromeconate resembled the meconate; the red acetate bore similar testimony; the blue solution of the ferric ferrocyanide in oxalic acid gave results fully corroborative of the influence both of the nature and of the mass of every substance present at the same time in the mixture; the purple and the red comenamate afforded similar results; while the red bromide (not the oxybromide), though somewhat indistinct in its testimony, corroborated to a certain extent the preceding observations.

Experiments were performed with a view to determine what effect the mass of water might have on the salts operated upon; its influence in reducing the colour of the ferric sulphocyanide was found to be very great, but the nature of it could not be exactly determined. As however it was uniform in its action in whatever manner the sulphocyanide had been produced, it could not affect the results of the preceding experiments. Water did not appear to act in any similar manner upon the other ferric salts.

From the mass of quantitative observations made during the investigation, it was possible to deduce not only the order of affinity of the various acids for sesquioxide of iron as compared with potash, but also to assign approximative numbers. Doubt may rest on the position of some terms in the series, but hydrosulphocyanic acid certainly had the least affinity for ferric oxide in comparison with potash: it was represented by unity: the other acids followed in the order—nitric, 4; hydrochloric, 5; sulphuric, 7; gallic, 10; pyromeconic; meconic; acetic, 20; hydrobromic; comenamic; citric, 100; hydroferrocyanic, 170.

Other coloured salts were submitted to a more cursory investigation. The scarlet bromide of gold when treated with an alkaline chloride gave a striking instance of the effect of mass in gradually overcoming a strong affinity. The intensely red iodide of platinum afforded results which, though somewhat obscure, were not opposed in their testimony. So did the blue sulphate of copper when treated with different chlorides. The "manganoso-manganic oxide" dissolves in sulphuric or phosphoric acid of a red, and in other acids of a deep brown colour; and it was found that hydrochloric acid was capable of changing the colour of the sulphate according to its mass, while on the other hand sulphuric or phosphoric acid altered in like manner the tint of the chloride. Somewhat similar results were obtained by means of the green chloride and the purple fluoride of molybdenum; and the blue solution that forms when gallic acid is brought in contact with both the oxides of iron at once, bore testimony to the same general laws. The peculiar optical character of certain salts of quinine was also taken advantage of for determining what changes took place among the compounds in solution. The amount of fluorescence exhibited by a solution of acid sulphate of quinine was found to be affected by the admixture of a chloride, bromide, or iodide according to the nature and the mass of the salt added, and the addition of sulphuric, phosphoric, nitric and other acids was found to produce a fluorescence in solutions either

of hydrochlorate of quinine, or of sulphate which had been rendered non-fluorescent by hydrochloric acid. Similar results were obtained with quinidine; and somewhat analogous ones with the organic bases contained in horse-chestnut bark, and in tincture of stramonium. An experiment is also narrated showing that the same laws hold good in respect to compound ethers as to salts having metallic bases, alcohol being employed as the solvent.

Beside the very diversified substances already mentioned in this abstract, several others, such as lead, mercury, zinc, potash, soda, baryta, lime, and ammonia, are shown by a more indirect proof to enter into compounds which obey the same laws. Hence it is concluded that what was observed in reference to the ferric salts holds good very generally, if not universally.

The bearing of certain other phenomena upon the question at issue was also examined. The fact that precipitation, when it occurs, gives rise to a perfect interchange of bases and acids, is equally consistent with either Bergmann's or Berthollet's theory; but not so is the fact that two soluble salts cannot be mixed without the occurrence of precipitation, if one of the products that may be formed is an insoluble salt. The only recorded exception to this law, which occurs with oxalate of iron in the presence of a salt of yttria, under peculiar circumstances, was found on close examination to be in perfect accordance with the principles laid down by Berthollet. Besides the argument founded on this universal fact, several experiments were devised for the purpose of proving that the complete precipitation of an insoluble salt on the mixing of two soluble salts, was due to the insoluble compound being removed at once out of the field of action on the first distribution of the elements, thus necessitating a redivision, and so on until no more of it could possibly be formed. The phenomena attending volatilization have the same bearing as those connected with precipitation. If by the mutual action of two salts a substance be formed, which, though soluble in water, requires more water for its solution than is present, it crystallizes out: certain experiments were noted where this action occurs, and it was found that they gave testimony in favour of the same views as have been supported by the preceding observations. The bearing of the phenomenon of diffusion of salts upon the point at issue was also examined: Malaguti's experiments were discussed; and they, as well as some observations on the solution of certain bodies by others set at liberty, were found to bear testimony also in the same direction.

During the whole of the experiments on this subject, most of which were performed quantitatively, no unequivocal instance occurred of two substances having so strong an affinity for one another, that they combined to the exclusion of other bodies of like kind present in the same solution. After showing that some reputed exceptions are really not capable of being proved to be so, and after suggesting some probable limitations of the action of the general law, the paper concludes with the following deductions:—

I. That where two or more binary compounds are mixed under

such circumstances that all the resulting compounds are free to act and react, each electro-positive element enters into combination with each electro-negative element in certain constant proportions.

II. That these proportions are independent of the manner in which the different elements were primarily arranged.

III. That these proportions are not merely the resultant of the various strengths of affinity of the several substances for each other, but are dependent also on the mass of each of the substances present in the mixture.

IV. That an alteration in the mass of any one of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regular progressive ratio; sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion.

V. That this equilibrium of affinities arranges itself in most cases in an inappreciably short space of time, but that in certain instances the elements do not attain their final state of combination for hours.

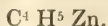
VI. That totally different phenomena present themselves where precipitation, volatilization, crystallization, and perhaps other actions occur, simply because one of the substances is thus removed from the field of action, and the equilibrium that was first established is thus destroyed.

VII. That consequently there is a fundamental error in all attempts to determine the relative strength of affinity by precipitation,—in all methods of quantitative analysis founded on the colour of a solution in which colourless salts are also present,—and in all conclusions as to what substances exist in a solution, drawn from such empirical rules as, that “the strongest acid combines with the strongest base.”

March 15, 1855. (The Lord Wrottesley, President, in the Chair.)

“Researches on Organo-metallic Bodies.” By E. Frankland, Ph.D., F.R.S. Second Memoir.—Zincethyle.

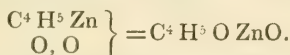
This compound, whose existence was mentioned in a previous memoir*, is formed by the action of zinc upon iodide of ethyle, or a mixture of iodide of ethyle and anhydrous ether, at a temperature exceeding 100° C. The materials are enclosed in a copper digester capable of resisting great pressure. When purified by rectification in an atmosphere of carbonic acid, zincethyle possesses the following properties:—At ordinary temperatures it is a colourless, transparent and mobile liquid, refracting light strongly and possessing a peculiar odour, rather pleasant than otherwise, and therefore differing greatly from that of zincmethyle. Its specific gravity is 1·182 at 18° C. Exposed to a cold of −22° C. it exhibits no tendency to become solid. Zincethyle boils at 118° C., and distils unchanged. The specific gravity of its vapour is 4·251. Several analyses of zincethyle prove its formula to be



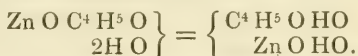
* Philosophical Transactions, 1852, p. 436.

The vapour volume of zincethyle is highly remarkable, and almost compels us to conclude that the vapour volume of the double atom of zinc is only equal to that of oxygen, instead of corresponding with the volume of hydrogen, in accordance with the generally received supposition. Zincethyle, therefore, appears to belong to the so-called water type, and to consist of two volumes of ethyle and one volume of zinc vapour; the three volumes being condensed to two: for if we were to assume that an equivalent of zinc occupies the same vapour volume as an equivalent of hydrogen, we should then have the anomaly of the combination of equal volumes of two radicals being attended by condensation.

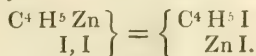
Although zincethyle is remarkable for the intense energy of its affinities, which place it nearly at the head of the list of electro-positive bodies, yet it does not appear to be capable of forming any true compounds with electro-negative elements, its reactions being all double decompositions in which the constituents of the zincethyle separate. Zincethyle is spontaneously inflammable in atmospheric air or oxygen; but when a few drops, diluted with ether to prevent inflammation, are passed into a mercurial eudiometer containing dry atmospheric air, a rapid absorption of oxygen takes place, with the formation of a white amorphous solid composed of zinc, ethyle, and oxygen. This reaction, which is also common to zincmethyle and zincamyle, led me to suppose that, like cacodyle, these bodies combined directly with oxygen; but the results of a closer study of the action of oxygen upon zincethyle prove that no such compound is formed; the white body being ethylate of zinc, and containing no organo-metallic compound, in the strict sense of the term. The action of oxygen upon zincethyle is expressed in the following equation:—



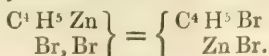
The ethylate of zinc thus produced is decomposed by water into hydrated oxide of zinc and alcohol—



Zincethyle is acted upon with great energy by iodine; when the violence of the reaction is moderated, by the application of intense cold and the intervention of ether, the sole products are iodide of zinc and iodide of ethyle—

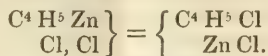


Bromine acts with explosive violence on zincethyle, but the action may be moderated by adding the bromine in the form of diffused vapour and cooling to 0° C. The sole products of the reaction are then bromide of ethyle and bromide of zinc—

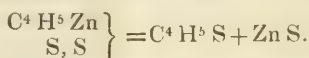


Zincethyle burns with a lurid flame spontaneously in chlorine gas;

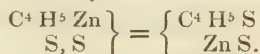
the zinc and hydrogen are converted into chlorides, whilst carbon is deposited in the form of soot. I have not studied the products of a more moderate action, as it is difficult to bring the materials together without too great an elevation of temperature. There can be no doubt, however, that the moderated action of chlorine would be analogous to that of bromine or iodine, and that the products would be chloride of ethyle and chloride of zinc—



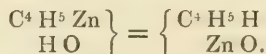
Carefully dried flowers of sulphur have only a slight action upon an ethereal solution of zincethyle, but the application of a gentle heat suffices to produce a brisk reaction; the sulphur gradually disappears, a white flocculent precipitate is formed, and a strong odour of sulphide of ethyle developed. The chief product of this reaction is the double sulphide of ethyle and zinc (mercaptide of zinc), which is produced as follows:—



A little free sulphide of ethyle is also formed—



Finally, zincethyle is decomposed by water into oxide of zinc and hydride of ethyle—



It is also similarly acted upon by the hydrated acids and by the hydrogen compounds of chlorine, bromine, iodine, fluorine and sulphur.

The behaviour of zincethyle in contact with the electro-negative elements is highly remarkable, and cannot fail to have an important influence upon our views of the condition of bodies at the moment of chemical change,—a subject so ably discussed by Brodie*, whose ingenious views I consider to receive a new support in these reactions of zincethyle, by the singular way in which ethyle, a body low down in the electro-positive series, unites with oxygen, chlorine, &c., in the presence of a large excess of the intensely electro-positive zincethyle. This behaviour also strikingly confirms the suggestions I ventured to make in my former memoir†, relative to the moleculo-symmetrical form of organo-metallic compounds. In the inorganic combinations of zinc, this metal unites with one atom only of other elements; a very unstable peroxide, not hitherto isolated, being the only exception. The atom of zinc appears, therefore, to have only one point of attraction, and hence, notwithstanding the intense affinities of its compound with ethyle, any union with a second body is necessarily attended by the expulsion of the ethyle.

* Philosophical Transactions, 1850, p. 789.

† Ibid. 1852, p. 438.

THE CHEMICAL GAZETTE.

No. CCCI.—May 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Saponification of Oils under the influence of the Substances which accompany them in Seeds. By J. PELOUZE.

SINCE the researches of M. Chevreul have assimilated fatty bodies to æthers or salts, and made known their decomposition into particular acids and glycerine by the action of hydrated alkalies, it was easy to foresee that analogous reactions would occur under other circumstances. Thus M. Fremy has shown that the oils and neutral fatty bodies in general are entirely converted into fatty acids by concentrated sulphuric acid. The previous union of this acid with the oleic and margaric acids and glycerine does not at all diminish the final distinctness of the phænomenon of saponification. Beyond these two methods for the saponification of fatty bodies by bases and by acids, nothing certain has hitherto been stated regarding their acidification by other agents. I must however indicate the state of the question at the period when I commenced its study:—

“The foreign substances with which fatty bodies are contaminated exert the same action upon them that a ferment does upon saccharine fluids; the alteration which they undergo excites the decomposition of the glyceric compounds, the fatty acids are set free, as well as the oxide of glyceryle, which sometimes separates without decomposition, as in palm-oil, but is usually decomposed.” (Liebig, Organic Chemistry.) “The circumstances necessary for the fermentation of fatty matters are the same as those which occur in all fermentations. It requires the concurrence of an albuminoid body, water, air, and a temperature of from 59° to 86° F. Under these circumstances the substance becomes heated, and soon acquires all the properties of a rancid grease.” (Dumas, *Traité de Chimie*.) “Inodorous and tasteless oils, when in contact with air and moisture, acquire a disagreeable odour and a very persistent taste. Fleishy oleaginous fruits and crushed oleaginous seeds undergo a true fermentation, the result of which is the disunion of the acids and glycerine. I have had occasion to observe a similar production of free acid during the putrefaction of seeds containing much fatty matter.” (Boussingault, *Economie Rurale*.)

M. Bernard has proved that the pancreatic sugar rapidly resolves neutral fatty bodies into acids and glycerine. (*Comptes Rendus, Chem. Gaz.* 1855. K

xxviii. p. 249 and 283.) M. Berthelot, in his thesis, says a few words on the acidification of neutral fatty matters, either natural or artificial, when in contact with the air; he attributes this transformation to the moisture of the atmosphere, and compares it with the decomposition which these same bodies undergo in closed vessels, by the action of water at a high temperature. Lastly, I may mention that seventeen years ago, M. Boudet and myself ascertained that the palm-oil of commerce is a mixture of glycerine, of neutral fatty matter and of acid, the proportion of the latter amounting sometimes to four-fifths of the weight of the oil.

I will not speak here of the slow alteration which fatty matters undergo in the air; this phenomenon, which is still so obscure, appears also to have only a very distant relation with true saponification; it is accompanied by an absorption of oxygen and an evolution of carbonic acid, which do not take place in saponification. The facts of which I am about to present an analysis indicate a very distinct resolution of fatty bodies into acids and glycerine, without the intervention of air. They may be stated shortly as follows:—

When oleaginous seeds are crushed, so as to break up their cells and bring the substances of which they are composed into close contact, the neutral fatty bodies contained in these seeds are converted into fatty acids and glycerine. In this case there is something analogous to what takes place in the grape, the apple, and many other fruits, the sugar contained in which is converted into alcohol and carbonic acid as soon as the cells which separate it from the ferment are destroyed.

Linseed, seeds of rape, mustard, poppy, groundnut, sesame, camelina and chamomile, nuts, walnuts, and sweet and bitter almonds, were pounded in a mortar; the oil taken from them *immediately*, either by pressure or by means of æther or benzine, did not contain any fatty acids, or only contained traces of them. This first series of experiments, repeated several times, proved that seeds at the moment of division contained the whole of their fatty matter in a neutral state. This agrees with what is generally supposed.

At my desire, M. Bouquet, the director of M. Menier's large chemical establishments, caused a certain quantity of the greater part of the above-mentioned seeds to be ground to meal in his own presence, and sent me portions of this flour packed in earthen vessels stopped with corks. In a few days I found that the whole of these flours contained considerable quantities of glycerine and fatty acids, which went on constantly increasing for several months. The bruised seeds being kept in closed vessels, there was every reason to think that the air had nothing to do with this reaction. I confirmed this supposition by bruising some of the seeds in which this sort of spontaneous saponification took place most readily, putting them into glass bottles, which they filled completely, and closing them with care. In a few days I obtained quantities of fatty acids, which were always readily appreciable, and sometimes considerable. Thus walnuts, reduced to a paste and kept for five days at a temperature of 50° to 77° F., furnished an oil containing 9 per

cent. of its weight of fatty acids; and another sample, which was kept eight days, gave 15 per cent. Oil of sesame in eight days gave 6 per cent., in a month 17.5 per cent, and in three months 47.5 per cent. of fatty acids. Poppy-oil furnished nearly the same results. Sweet almonds, kept for three weeks, furnished an oil containing only $3\frac{1}{2}$ per cent. of fatty acid; and groundnut oil at the end of a month contained 6.3 per cent., and in three months 14 per cent. Linseed and rapeseed, kept for three weeks, furnished an oil containing 5 and 6 per cent. of fatty acids.

The saponification in question appears to vary in its intensity, not only with the temperature, but also with the quantities of bruised seeds employed. I have not yet met with an oil entirely saponified; the one which furnished the largest quantity of acid is poppy-oil. I kept some poppy-seeds reduced to powder for four months in an earthen vessel; they then furnished an oil containing 85 to 90 per cent. of fatty acid.

I pass now from simply-divided seeds to the cakes produced in the extraction of oils on a large scale; these all contain fatty acids, and if they be old, it almost always happens that they no longer contain oil, this having become entirely acidified. It would be interesting, in connexion with this complete transformation of the neutral fatty matters into acids, to ascertain their influence in the alimentation of cattle, and to follow it from the commencement of this spontaneous saponification, that is to say, from the moment when the seed, is crushed to the period of complete acidification. The oil-cakes contain, on an average, 10 per cent. of fatty matters, and it is not to be supposed that the neutral or acid state of these is a matter of indifference in the alimentation of animals.

When oleaginous seeds are reduced to powder and moistened with water, putrefaction commences in a few days, and they then exhale a fetid and strongly ammoniacal odour. Far from containing more fatty acid than seeds simply crushed, they contain a good deal less; and it appears that the ferment, or the organic matter whatever it may be that fulfils its office, is destroyed, and ceases to act upon the neutral oils. I have in vain endeavoured to isolate this matter.

In the course of my researches I have ascertained that the sugar which is contained in considerable quantity in walnuts, nuts, and sweet and bitter almonds, is identical with cane-sugar, and that these seeds contained no trace of glucose. Nearly the whole of the sugar remains in the cakes after the oil has been separated by expression. It is so abundant in the cake of the walnut, that when the latter is suspended in water with a little yeast, an active fermentation is set up in the mixture in a few moments, and this gives rise to a considerable quantity of alcohol, which may readily be separated by distillation.

In the determination of the proportion of fatty acids mixed with the oils, it is not sufficient to treat the mixture with absolute alcohol; this would lead to the most serious errors. I have, in fact, ascertained that in the presence of the fatty acids the neutral oils are able to dissolve in alcohol. When alcohol is mixed with oils, the addition

of oleic acid to the mixture causes the solution of the latter; and if the oleic acid be in great excess in proportion to the oil, the addition of fresh alcohol produces no turbidity in the mixture.

I have made an experiment upon saponification, which I shall mention here, although it has no connexion with what has gone before, because I think it may explain why potash and soda, which are such energetic bases, nevertheless saponify fatty bodies far more slowly than lime. It appeared probable that this depended upon the circumstance, that milk of lime mixes with fatty bodies far better than a solution of potash or soda. The following experiment renders this explanation very admissible. When a neutral oil is dissolved in hot alcohol, and an alcoholic solution of potash is added to it, the mixture, if brought to boiling, is instantly saponified; water does not separate from it the least trace of fatty matter, and the addition of muriatic acid to the solution furnishes fatty acids, which are completely soluble in alkalies and in alcohol. In the same way, if an oil be mixed with an excess of concentrated sulphuric acid, the saponification takes place instantaneously and completely; the whole of the oil is converted into sulpho-fatty acids and sulphoglyceric acid. In the two cases here referred to, the saponification is immediate, because the bodies brought in contact and those formed mix in all proportions, and thus present very numerous and intimate points of contact.

The saponification of neutral fatty bodies by potash or soda with alcohol instead of water as the solvent, might be usefully adopted in lectures, as it occupies almost less time in its realization than in its description; and hitherto this curious reaction, performed under ordinary conditions, required far too much time to be capable of execution, even on a very small scale, in the presence of an audience during a lecture. The same facility of execution applies also to the saponification of oils by concentrated sulphuric acid.

As I have mentioned the sulpho-fatty acids of M. Fremy, I may add that the residues of the purification of colza-oil are principally composed of these acids and sulphoglyceric acid. These residues, the price of which has almost suddenly risen from 5 francs to more than 60 francs per 100 kilogrms., are employed in tanning, and especially in the manufacture of beet-root alcohol, to destroy the froth produced during the fermentations. The manufacturers who make use of them should bear in mind that these residues are not, as they suppose, oil contaminated by the colouring and carbonaceous matters produced by the action of sulphuric acid upon colza-oil, but that they contain principally double acids, and that they cannot furnish fatty acids without at the same time eliminating a certain quantity of sulphuric acid. A sample of one of these residues, sent to me from Lille by M. Kuhlmann, was entirely soluble in cold water, although from its appearance it might have been mistaken for oil. M. Thenard, who is the founder of the system of purifying lamp-oils, now become one of the principal industries of the northern departments, observed that the purification does not take place well except with very concentrated sulphuric acid; this circumstance is

now explained by our exact knowledge of the nature of the residue of the purification.

The new facts contained in the memoir of which the preceding is an abstract, are not without their application. Thus linseed-meal is either neutral or acid according as it is new or old, and must consequently act differently as a medicament. That which has long been prepared must be rejected, even though it may have been kept in well-closed vessels. I have several times found linseed-meal in the shops in which all the oil was completely acidified. Milk of almonds, freshly prepared, contains neutral oil of almonds; by the following day acidification has already commenced. Any edible oil will have a different composition and taste, according to the length of time that has elapsed before the seed from which it has been extracted was submitted to pressure. The best oils for the table are those which have been extracted immediately after the crushing of the seed.

Old oil-cakes may be advantageously employed in the manufacture of an economical soap. All that is necessary is to mix them with an alkaline solution; but the quantity prepared must be small, as the albuminoid matter contained in them begins to decompose in about a fortnight, producing a very disagreeable odour.—*Comptes Rendus*, March 19, 1855, p. 605.

On the Action of Heat upon the Acetates of Iron.

By L. PÉAN DE ST. GILLES.

In a memoir read before the Philosophical Society of Glasgow, Mr. Walter Crum has pointed out the existence of a remarkable allotropic modification of the hydrate of alumina, soluble in pure water, and extracted from the acetate, which was decomposed by exposure to a temperature of about 212° F. for about ten days. Having had occasion to study the reactions of the acetates of iron, I performed some analogous experiments; and in opposition to the opinion put forward by the author of the paper just mentioned, I succeeded in preparing by double decomposition an acetate of iron, which did not furnish any precipitate at a boiling heat. Want of space prevents my describing the mode of preparation of this compound, as well as several of its characters. I shall only state, that when heated in contact with a very small proportion of sulphate of iron or of an alkaline salt, it deposits the whole of its hydrated oxide of iron in an insoluble state.

I pass at once to the prolonged action of heat, which has led Mr. Walter Crum to the discovery of the soluble hydrate of alumina. Having placed a solution of pure acetate of iron in a water-bath heated to the boiling-point, I found that in the course of four or five hours the liquid became opaline, and appeared turbid by reflected light, whilst, when examined by transmitted light, it appeared transparent; at the same time, its colour, which had previously been that of venous blood, became brick-red, but without any diminution of intensity. This condition was permanent, remaining even after

cooling, and the liquid deposited nothing even when it had stood several days. After heating it thus for twenty-five or thirty (not consecutive) hours, I submitted it to examination. It had completely lost the metallic taste of the salts of iron, and acquired that of vinegar; when boiled in a thin uncovered vessel, it gave off a large quantity of acetic acid, and remained limpid for some time; but in the course of an hour and a half or two hours, the hydrated oxide of iron was completely deposited. It was impossible therefore to obtain the soluble modification of this hydrate by the process which Mr. Walter Crum had applied to alumina; nevertheless the study of the properties of the acetate thus transformed soon furnished me with quite unexpected results; in fact, it no longer presents the characters of the salts of iron. Sulphocyanide of potassium does not heighten its tint, whilst it reddens the solution of the ordinary acetate very strongly. The ferrocyanide, like all the other salts of potash, forms in it a brownish ochreous precipitate, which acquires a greenish tinge by long contact. A trace of sulphuric acid or of an alkaline salt precipitates all the iron in the form of a reddish-brown deposit, which is insoluble in all cold acids even when concentrated. It is dissolved by boiling muriatic acid, but is not acted upon by nitric acid.

When the liquid is poured into muriatic or nitric acid, a brick-red granular precipitate is thrown down, which collects at the bottom of the vessel, and cakes together very easily. This precipitate, which has no resemblance in its form to the ordinary hydrated oxide of iron, may be washed without alteration with the same acids, however concentrated they may be, or even with nitromuriatic acid; but if by one or two decantations with distilled water the mother-liquor be freed from the greater part of the acid which it contains, the precipitate disappears entirely, and a brick-red opaline liquid, exactly like that formed by the modified acetate, is produced. In this manner an indefinite number of alternate precipitations and solutions may be effected by the employment of muriatic or nitric acid; but if any other acid (except acetic acid) be substituted, the deposit, when once formed, does not dissolve again in pure water.

This new and singular substance is not precipitated by ordinary alcohol, muriatic and nitric acids diluted with water, acetic acid of any degree of concentration, or by the acetates of alumina, iron or chromium. To free it from the acetic acid which dissolved it in the first place, I precipitated it with muriatic acid; but I have not hitherto been able to separate the latter acid completely, or to prepare a purely aqueous solution of the ferric compound. Nevertheless, by turning the precipitate upon a plate of unglazed porcelain, I obtained the substance in the form of a moist varnish, and only slightly acid, the mother-liquor being almost entirely absorbed. In this state it was entirely soluble in pure water, and possessed no appreciable taste; when dried *in vacuo*, it lost its power of dissolving.

The watery solution, when boiled, also deposits insoluble hydrated oxide of iron. Acetic acid prevents this precipitation, which explains

why I could not entirely drive off this acid by ebullition, without at the same time causing the separation of the iron.

The opaque appearance presented by the acetate when modified by heat and viewed by reflected light, might raise a doubt as to whether this liquid is a true solution; and although under the microscope, with a power of 200 diameters, it appears completely homogeneous, we may well suppose that the iron compound may exist in it in a peculiar state, perhaps comparable to that of prussian blue dissolved in oxalic acid. In other respects it is perfectly fluid, may be congealed without alteration, and filters very easily through paper washed with acidulated water, to free it from the calcareous salts with which it is always impregnated. The characters of the liquid are consequently those of a real solution; and even if this term should not exactly express its nature, it appears to me to be the only one by which we can at present describe the very peculiar phenomena which it presents.

Such are the general results at which I have already arrived with regard to the acetates of iron. Although the facts observed, and the analogies existing between these reactions and those of alumina, appear to concur in proving the existence of an allotropic modification of hydrated oxide of iron, I hesitate to give an opinion upon this subject until I have exactly determined the composition of this compound. I have forwarded a quantity of it to a friend who has undertaken to study its therapeutical properties.—*Comptes Rendus*, March 12, 1855, p. 568.

Note on a new method of Biting for Heliographic Engraving upon Steel. By NIEPCE DE SAINT-VICTOR.

The author has been engaged in researches with a view to obtain a substitute for nitric acid in heliographic engraving upon steel. The fumigations indicated by him often give too much or too little resistance to the varnish, so that it was necessary to find some mordant which would act upon the metal without attacking the varnish.

For this purpose he has found nothing better than water saturated with iodine at a temperature of 50° – 59° F. at the outside, so that it may have a golden-yellow colour with no trace of reddish-orange.

The biting is commenced by covering the plate with iodized water, which is renewed in ten minutes or a quarter of an hour; a part has then combined with the steel to form iodide of iron, and the other is volatilized, so that it is important to change the iodized water two or three times, that is to say, until the plate is considered to be sufficiently bitten.

The biting takes place slowly, and is never deep enough, unless the operation is completed by water slightly acidulated with nitric acid; it has then sufficient action to eat into the metal to a greater depth than the iodine, without however attacking the ground. The application of this method has given excellent results.—*Comptes Rendus*, March 12, 1855, p. 584.

*On the Compounds of the Acetones with Alkaline Bisulphites.**By Dr. LIMPRICHT.*

Bertagnini's discovery, that the aldehydes form crystallizable compounds with the alkaline bisulphites, is certainly one of the most promising that has been made recently. From the insolubility of these compounds in a saturated solution of alkaline bisulphites, they may be very advantageously employed in the preparation of the pure aldehydes; and if the property of combining with the alkaline bisulphites belonged *only* to the aldehydes (and Bertagnini could not obtain similar compounds with any other organic body), we should at once possess a characteristic reagent for all bodies belonging to this group of substances. Some of my experiments however prove that the acetones exhibit a similar behaviour.

I have particularly examined only the compounds of the acetone of acetic acid with alkaline bisulphites:—

1. Pure acetone, agitated with a concentrated solution of bisulphite of soda, dissolves with considerable evolution of heat, and on cooling, laminar crystals of sulphite of acetone and soda separate. They dissolve pretty readily in water, with more difficulty in alcohol; when heated by themselves, they evolve empyreumatic products; when distilled with a solution of an alkaline carbonate, pure acetone goes over. For analysis they were freed from mother-liquor by pressing between paper, and dried over sulphuric acid. Analysis gave:—

		Calculated.	Found.
C ⁶	36	22·2	21·3
H ⁷	7	4·3	4·1
O ³	24	14·8	15·7
NaO	31	19·1	19·2
S ² O ⁴	64	39·6	39·7

leading to the formula NaO, C⁶ H⁶ O², 2SO² + Aq.

2. The compound of acetone with bisulphite of potash is prepared in the same way as the soda compound, and resembles it in all its properties. Its composition is KO, C⁶ H⁶ O², 2SO². Found, 27·21 per cent.; calculated, 27·81 per cent. of potash.

3. If acetone be mixed with a very concentrated watery solution of bisulphite of ammonia, it dissolves with such a great evolution of heat that the mixture begins to boil; on cooling, however, no crystals are deposited. On evaporation, the compound remains in a solid form, but still mixed with bisulphite of ammonia. I did not take the trouble to prepare it pure.

Dr. Gössmann has lately stated, that by the distillation of sulphite of aldehyde and ammonia with an excess of lime, he obtained æthylamine, and engages to investigate the behaviour of the other aldehydes in this respect. It became important therefore to make a similar experiment with the acetone compounds discovered by me. The sulphite of acetone and ammonia distilled with an excess of lime actually furnishes a volatile base, which may be separated from the ammonia which passes over at the same time by treating the dry

muriate with absolute alcohol. If the salt remaining after the evaporation of the alcoholic solution be mixed with potash, a very penetrating ammoniacal odour is evolved; and if this experiment be performed in a small glass tube, the gas produced may be ignited. I am still occupied with the investigation of this base.

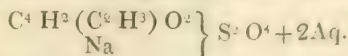
By the distillation of butyrate and valerianate of lime, butyral and butyrone, valeral and valerone are obtained amongst other products. If these mixed products of distillation be agitated with an alkaline bisulphite, the fluid sets after some time into a crystalline jelly, which was pressed between paper and dried over sulphuric acid. Analyses gave numbers which showed that in the one case this was a mixture of compounds of butyral and butyrone, and in the other of valeral and valerone, with the alkaline bisulphite. Although the composition and properties of the isolated compounds were not determined in these experiments from the deficiency of material, it nevertheless appears that butyrone and valerone behave like the acetone of acetic acid with alkaline bisulphites, and that this may be asserted with great probability of all the acetones; and also that butyral and valeral, which, on account of their boiling-point and behaviour, are considered not to be identical with the true aldehydes of butyric and valerianic acids, certainly approach very closely to the aldehydes in their behaviour towards the alkaline bisulphites.

It appears to me that the compounds of the acetones with alkaline bisulphites may throw some light upon the rational formula of the former. Gerhardt, whose views are very justly becoming more and more appreciated by chemists, derives the aldehydes from the hydrogen type $\left. \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} \right\}$, in which 1 atom is replaced, in the case of acetic

aldehyde for example, by the radical acetyloxy, $\left. \begin{smallmatrix} \text{C}^4 \text{H}^3 \text{O}^2 \\ \text{H} \end{smallmatrix} \right\}$. In the compounds of this with alkaline bisulphites, the other atom of hydrogen is replaced by the alkaline metal, thus $\left. \begin{smallmatrix} \text{C}^4 \text{H}^3 \text{O}^2 \\ \text{K} \end{smallmatrix} \right\} \text{S}^2 \text{O}^4$.

The acetones are derived from the same type, and are to be regarded as aldehydes in which the place of the second atom of hydrogen has been taken by an alcoholic radical, thus $\left. \begin{smallmatrix} \text{C}^4 \text{H}^3 \text{O}^2 \\ \text{C}^2 \text{H}^3 \end{smallmatrix} \right\}$. According to this view, however, the production of the compounds of the alkaline bisulphites with the acetones cannot be explained, since the place of the atom of hydrogen which should have been displaced by the alkaline metal is already taken by an alcoholic radical.

But if the formula of acetone be written $\left. \begin{smallmatrix} \text{C}^4 \text{H}^2 (\text{C}^2 \text{H}^3) \text{O}^2 \\ \text{H} \end{smallmatrix} \right\} -$ just as in the oil of *Gaultheria* the methyle of the acid radical takes up 1 atom of hydrogen—this difficulty is got rid of, and the rational formula for the sulphite of acetone and soda will be—



*On the Products of the Distillation of Stearic Acid.**By Prof. HEINTZ.*

Chevreul has stated that stearic acid is capable of being distilled without decomposition, and that it only gives rise to a small quantity of products of distillation, amongst which the principal are carbonic acid, water and hydruret of carbon. Redtenbacher, on the contrary, concluded from his experiments, that in this operation margaric acid, margarone, carbonic acid, water, and hydrocarbons are formed from stearic acid. As, according to the author's previous investigations, margaric acid does not exist as a chemically pure substance, and as it has been quite recently asserted by Laurent and Gerhardt, that under favourable circumstances stearic acid may be distilled entirely without decomposition, the author was induced to repeat Redtenbacher's experiments. He effected the distillation in a current of hydrogen, and separated its products even in the first distilling apparatus into three portions, of which one was solid at ordinary temperatures, and did not distil over at 302°F. ; the second was separated from the first by elevating the temperature to 302°F. , and was collected in a fluid form; whilst the third was collected in a gaseous form. In this last portion the author distinctly detected carbonic acid.

The fluid portion consisted of an aqueous and an oily stratum. The former contained acetic acid and a small quantity of an acid containing more carbon, belonging to the series of fatty acids, probably butyric acid, which the fluid resembled in its odour. The oily stratum, on the contrary, when analysed, gave numbers corresponding to the formula $\text{C}^{70}\text{H}^{70}\text{O}$. There was consequently no doubt that it was a mixture of several substances, probably of hydrocarbons (C^mH^m) and cetones ($\text{C}^n\text{H}^n\text{O}$). The solid distillate could be separated into a fatty acid and neutral products, of which the former was nearly pure stearic acid, as it fused at $155^{\circ}\cdot3\text{F.}$ By a single recrystallization, its melting-point rose immediately to $156^{\circ}\cdot5\text{F.}$, the melting-point of pure stearic acid, with which it agreed perfectly. The alcoholic fluid pressed from it contained, besides stearic acid, a small quantity of a more solid, but more readily fusible acid of the fatty acid series. The neutral part of the solid products of distillation contained a substance which melted at $191^{\circ}\cdot3\text{F.}$, and was very difficult of solution in cold æther, together with another solid, but more soluble and fusible substance and fluid oleaginous bodies. Of none of these substances was a sufficient quantity obtained for an elementary analysis.

The fluid products were submitted to fractional distillation, by which the boiling-point was gradually raised, and the portions obtained deposited solid matters on cooling the more readily the later they were collected. The last distillate only contained $0\cdot8\text{--}0\cdot9$ per cent. of oxygen, and therefore consisted principally of hydrocarbons. As it contained the same number of equivalents of carbon and hydrogen, this substance may also be regarded as a mixture of hydrocarbons (C^mH^m) with cetones ($\text{C}^n\text{H}^n\text{O}$). The residue in the

retort contained no considerable quantity of acid constituents. It consisted essentially of the same substances which were found in the neutral portion of the solid distillate. Of the least fusible matter however it contained so much as to enable an analysis to be made, from which it appeared that this substance was the stearine ($C^{35}H^{35}O$) of Bussy.

From the results of these experiments the author arrives at the conclusion, that in the distillation of stearic acid the greater part passes over unchanged, but that a portion is decomposed in two different ways. Thus the decomposition takes place partly in such a manner, that acids of the fatty acid series with a smaller amount of carbon than stearic acid are produced, with separation of hydrocarbons (C^nH^n), and partly so as to give rise to carbonic acid, water and stearine. The stearine is also partly decomposed during the distillation, forming hydrocarbons and other more volatile cetones, containing less carbon. These decompositions may be rendered more intelligible by the following equations:—

1. $C^{36}H^{36}O^4 = C^nH^nO^4 + C^{(36-n)}H^{(36-n)}.$
2. $C^{36}H^{36}O^4 = CO^2 + HO + C^{35}H^{35}O.$
3. $C^{35}H^{35}O = C^nH^mO + C^{(35-m)}H^{(35-m)}.$

Monatsber. der Akad. der Wiss. zu Berlin, 1855, p. 5.

On Hydrated Protoperoxide of Manganese. By J. OTTO.

When an excess of ammonia is added to a solution of protochloride of manganese, which contains a sufficient quantity of muriate of ammonia to prevent it being precipitated by the ammonia, the mixture becomes turbid when exposed to the air, and deposits a brown oxide. This is usually said to be peroxide of manganese, but it really consists of a very interesting hydrate of the protoperoxide, MnO, Mn^2O^3 .

All the higher oxides of manganese furnish protoperoxide of manganese (red oxide) when calcined, and from this the quantity of manganese may be calculated. The oxygen, which exists in this compound in addition to the equivalent of the manganese, may be determined volumetrically, in a few minutes, by means of a solution of iron and muriatic acid and Marguerite's test-fluid (solution of permanganate of potash), the amount of water when the original oxides were hydrates may be calculated from the difference. Thus the whole analysis consists in a calcination and a volumetric testing.

The following example will explain the volumetric process:—0.953 grm. of freshly-calcined protoperoxide of manganese were dissolved by digestion in a solution of 0.6 grm. of iron wire in muriatic acid, which was freed from perchloride by zinc. The solution was much diluted, and the test-fluid was then added until the characteristic colour made its appearance; for this, 32 degrees of the test-fluid were required. Its constitution was such that 24 degrees of it represented 0.1 grm. of iron, and therefore 0.01428 grm. of oxygen. The excess of the oxygen in the protoperoxide of manganese had consequently converted into chloride as much of the 0.6

gram. of iron (=144 degrees of test-fluid) as corresponds with 112 degrees of the test-fluid (144-32). 112 degrees of test-fluid = 0.0666 of oxygen, and from calculation 0.953 gram. of protoperoxide of manganese should contain 0.0664 gram. of oxygen in excess.

Hydrated protoperoxide of manganese is yellowish-brown, with a reddish-brown tinge. When fresh precipitated, it is nearly granular, and not gelatinous. It is not changed by boiling with solution of muriate of ammonia. Acids decompose it, even when diluted; protoxide of manganese is dissolved, and a brownish-black hydrate of the peroxide separates. When heated, it leaves anhydrous protoperoxide, the colour of which varies exceedingly according to the temperature to which it has been exposed. It is obtained yellow, of the colour and appearance of precipitated gold, brownish-yellow or reddish-brown. The amount of water is about 5 per cent. It may be known to be pure if two equal quantities, the one calcined the other not, require equal quantities of test-fluid.

The formation of the hydrated protoperoxide of manganese in the ammoniacal solution is immediately known, when the very finely divided dark precipitate, which makes its appearance in a few moments on the addition of the ammonia, becomes converted into a far more voluminous, well-separated, paler precipitate. The dark precipitate is probably hydrated peroxide of manganese, which takes up protoxide from the fluid. If an open flask be half-filled with the solution, and left long enough in contact with the air, the ammonia being replaced as it evaporates, the fluid will become perfectly free of manganese, and at the bottom of the flask there is a rather dense, brown, pulverulent deposit, mixed with dark scales. These scales are produced in the form of a dark coat upon the walls of a flask, from which they are detached when the flask is shaken. A coherent crust is also formed on the surface of the fluid.

The deposit thus obtained is not perfectly pure hydrate of protoperoxide of manganese; it contains also protocarbonate of manganese, and small quantities of a higher oxide, of which it is possible the scales may be composed. The carbonate may be got rid of by boiling with muriate of ammonia; it dissolves as protochloride of manganese, whilst the ammonia escapes; but the higher oxide, in the state in which it exists here, does not appear to be capable of being entirely converted into the protoperoxide. The colour of the preparation thus obtained is not quite clean and bright. In the analysis of a preparation, which was obtained by allowing an ammoniacal solution of manganese to stand for two months, and boiled with solution of muriate of ammonia as long as there was any escape of ammonia, 1 gram. when calcined required 57 degrees, in the uncalcined state 56 degrees, of the test-fluid, which may almost be regarded as a perfect agreement.

When hydrated peroxide of manganese is put into an ammoniacal solution of protochloride of manganese, and gradually heated, the black peroxide is suddenly converted at a certain temperature into beautiful brown hydrate of protoperoxide. This is the most convenient mode of preparing this substance. The hydrated peroxide must either be freshly prepared and damp, or triturated with water,

before it is employed, as the conversion does not take place in the caked mass.

The best mode of preparing the hydrated peroxide is as follows. Carbonate of soda is added to a solution of protochloride of manganese until all the manganese is thrown down in the form of protocarbonate; an excess of the carbonate of soda is then added, and chlorine gas is passed into the fluid until it smells strongly of chlorine. The blackish-brown hydrated peroxide thus produced is then washed superficially by decantation, the first water being acidulated with nitric acid so as to get rid of any remains of the protocarbonate of manganese. The wet paste, mixed with ammonia until it has an alkaline reaction, is particularly adapted for our purpose.

Ammonia is now added in excess to a solution of protochloride of manganese containing muriate of ammonia; the fluid is quickly filtered from the flakes which always separate, and the blackish-brown paste of hydrated peroxide is added gradually. With a sufficient quantity of this, every trace of manganese may be thrown down from the solution; but as, in that case, it would be impossible to avoid an excess of the peroxide, a portion of the chloride must be left undecomposed. Small portions of the fluid are therefore filtered from time to time, and tested with sulphuret of ammonium, to see how much of the salt of manganese is still left*. The preparation is complete in a few minutes. The protoperoxide is deposited from the fluid with great rapidity, and may consequently be quickly washed. It has a bright yellowish-brown colour, and the properties which I have described above.

I have called this preparation a hydrate of the protoperoxide of manganese, because it corresponds with Wöhler's hydrate of protoperoxide of iron, and because the anhydrous red oxide is regarded as analogous to the magnetic iron ore. But its production in the last-mentioned manner, as well as its decomposition into protoxide and peroxide by the action of acids, evidently render it most simple to regard it as a compound of protoxide and peroxide. Thus $\text{MnO}, \text{Mn}^2\text{O}^3 = 2\text{MnO}, \text{MnO}^2$.

Hydrated peroxide of manganese is very readily deoxidized by sulphurous acid furnishing a solution of protosulphate of manganese. An ammoniacal solution of sulphite of ammonia however only reduces the peroxide to protoperoxide, and this takes place slowly at ordinary temperatures, but more quickly with the assistance of heat.

There can be no doubt that the blackish-brown hydrated oxide obtained by the action of chlorine, or rather of hypochlorous acid, upon protocarbonate of manganese is really hydrated peroxide, and it is also certain that no other degree of oxidation is produced at the same time, as might be supposed from Berthier's statements;

* The precipitate of sulphuret of manganese thus produced is of a beautiful flesh-colour when the fluid is perfectly free from iron; but the smallest trace of iron in a manganic solution causes it to give a white or grayish-white precipitate with sulphuret of ammonium, the red colour of the sulphuret of manganese being destroyed by the green of the sulphuret of iron.

but, notwithstanding all my care, I could not succeed in obtaining the oxide in such a form as to give me on analysis the calculated proportions of manganese and oxygen. The oxide has such powerfully oxidizing properties, that it can scarcely be protected from partial deoxidation. Even after the most careful washing, and when the wash-water no longer shows the least trace of acid, it acts on litmus-paper like a strong acid, from its producing acids by oxidation. In the analysis of some prepared with the greatest care, repeatedly washed with dilute nitric acid, and not dried upon paper, 1 grm. furnished 0.668 grm. of protoperoxide by calcination, representing 0.761 grm. of peroxide. From this the quantity of oxygen in excess may be calculated at 0.1396 grm. The volumetric test indicated 0.1237 grm. of oxygen, and the agreement is sufficiently close to leave no doubt as to its constitution. Thus to 10 equivs. of manganese there are 19 equivs. of oxygen, and it is consequently peroxide.—Liebig's *Annalen*, xciii. p. 372.

ANALYTICAL CHEMISTRY.

On the Volumetric Determination of Free Sulphuric Acid by means of a new Acidimetric Fluid, and on the employment of the latter in Acidimetric Determinations in general. By L. KIEFFER.

FOR the determination of free sulphuric acid in fluids by the following method, all the apparatus necessary consists of a few correct measuring vessels and a burette divided into cubic centimetres and tenths; and the only materials required are pure hydrate of sulphuric acid of spec. grav. 1.85, pure sulphate of copper, and some ammonia (ordinary ammonia of the shops).

A test-acid is first prepared by diluting the hydrate of sulphuric acid with water; the higher degrees of dilution, in which no diminution of volume or evaporation of the water by elevation of temperature takes place, are to be preferred.

5 cub. centims. of hydrated sulphuric acid are measured off with a pipette, and diluted with 75 cub. centims. of water. After the mixture has cooled, an acid of spec. grav. of 1.053, and containing 11.56 per cent. of acid, is obtained. This is preserved in well-stopped bottles.

The acidimetric fluid is then prepared by dissolving sulphate of copper in water, precipitating the solution by ammonia, and continuing the addition of the ammonia until the precipitate of hydrated oxide of copper is again dissolved. In this manner a fine azure-blue fluid is obtained; it is a solution of ammonia and oxide of copper and sulphate of ammonia. The former alone is acidimetric; the latter has no action. This fluid must now be valued by the test-acid in the following manner:—Exactly 5 cub. centims. of the test-acid are measured off in a pipette, and allowed to run into a test-glass; the pipette is then washed with water. The burette is then

filled with the solution of ammonia and oxide of copper, which, if the ammonia was not too weak, should have been diluted with a little water, and the mouth of the burette is closed with a cork pierced by a small glass tube, which is connected by a caoutchouc tube with a second short glass tube, so as to form a flexible mouth-piece. The tube of the burette is then held over the test-glass, and a thin stream of the fluid is caused to flow by blowing air into the open glass tube. The test-acid first becomes greenish, then bluish, from the formation of sulphate of copper. At length a few greenish clouds make their appearance, but disappear again by stirring. When this period has commenced, the ammoniacal solution of oxide of copper is added by drops and with the greatest caution, until a slight permanent turbidity is produced. The acid is then neutralized, and the slight turbidity indicates an excess of the precipitant, for which a deduction of about 0.05 cub. centim. may be made.

The per-centage strength of the test-acid being known, it follows that if the acidimetric fluid be of the right strength, 11.56 cub. centims. of it should have been employed. But if only 7 cub. centims. have been used, 4.6 vols. of water must be added to every 7 vols. of the test fluid, in order to obtain a fluid of which 1 cub. centim. indicates 1 per cent. by weight of hydrated sulphuric acid, if 5 cub. centims. of the acid under investigation be employed in the analysis. Greater exactitude is obtained by using a ten times diluted fluid towards the end of the analysis.

This method is perfectly volumetric, and no scales are required in any part of it. The author employs it in determining the free sulphuric acid existing together with acid metallic salts in galvanic batteries.

If weighing be combined with measurement, an equivalent of hydrated sulphuric acid may be weighed and diluted to a certain volume; the ammoniacal solution of oxide of copper is tested with a portion of this acid, and it will then serve to determine the per-centage contents in free acid of any other solution, if the operation be performed with a weighed quantity corresponding with its equivalent.

It is, of course, best to prepare the test-fluid as short a time as possible before each experiment; if kept, it must be well closed to prevent the escape of ammonia.—Liebig's *Annalen*, xciii. p. 386.

Description of a new Gas Furnace.

By PETER HART, *Manchester*.*

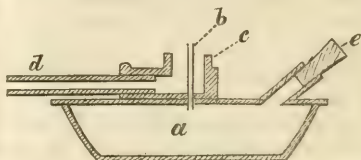
The apparatus I am about to describe was devised by me to answer the purpose of a Russian spirit-furnace, at the same time employing gas as fuel. Its leading feature, and the one in which I think it differs from most other gas furnaces, consists in the substitution of a jet of steam for one of compressed air. With this apparatus I can get a platinum crucible to a white-red heat in a few seconds, which is more than sufficient for all ordinary ignitions.

* Communicated by the Author.

fusions, and other analytical operations. When once set to work and properly regulated, it may be left to itself for a considerable time, thus sparing the operator the annoyance of standing by and working the blowing apparatus for half an hour; no bellows, or other such instrument, is required to work it; and lastly, it is so simple and inexpensive, that any tin-worker would, I think, be able to make one in at least a couple of hours.

My apparatus consists of a copper basin, *a*, about 5 inches in diameter; the edges are soldered down to a circular copper-plate, in the centre of which a small

hole is drilled; into this (to serve for a jet) is soldered one of the small copper tubes cut from a Leslie's patent gas-burner; this jet, *b*, is inserted into what in gas-fitters parlance is termed an elbow-joint



(this is better explained by examining *c* in the figure), standing exactly in the centre of the upright tube; this elbow-joint has screwed into it a short piece of ordinary gas-tubing, *d*, when this, together with a short tube for the purpose of admitting water, is soldered on, the apparatus is complete. To set it to work, fill the vessel *a* half-full of water, and set it in the ring of a retort-stand over a gas-flame, having first inserted a good cork into the short tube at *c*; then connect *d* by means of a length of india-rubber tubing with a supply of coal-gas; when the water boils, turn on the gas, and light it at *c*; the steam rushing through the jet *b* will produce with the flame an extremely hot brush of blue flame, exactly like the flame of a spirit-furnace; if the pressure is allowed to get too high, the flame will be blown out; of course the steam is regulated by increasing or diminishing the flame under the apparatus. A very few trials will enable the operator to discover the proportion of steam and gas which gives the most intense heat. Each time before using, the jet *b* should have a pin inserted into it, to see that it is not choked up, as when that happens to be the case, a very few moments suffice to get the steam sufficiently high to violently eject the cork, together with the whole of the water contained in the apparatus. In working with this as with a spirit-furnace, it is advisable to stand on the other side to that towards which the cork is likely to be driven.

PROCEEDINGS OF SOCIETIES.

Royal Institution.

Friday, March 16, 1855.

"On the Constitution of the Hydrocarbons." By Dr. William Odling, F.C.S.

Every chemical compound may be regarded in a great number of

different aspects. Each of the different theories that have been propounded concerning the chemical constitution of bodies, is true in reference to one particular aspect—untrue in reference to all others. Theories are of the highest service when they enable us to look upon a larger number of bodies from a single point of view—of the highest detriment when they prevent us from making use of all other points of view. To regard a body, or a class of bodies, exclusively in one aspect, or, in other words, to view all compounds by the light of a single theory, is necessarily to neglect a whole host of phænomena and relations. He has the most complete knowledge of a compound, who is capable of changing his position, and looking at the body from every possible point of view.

The theory of compound radicals is of the utmost service in enabling us to look upon a large class of bodies in one single aspect, in affording us one of the best means of arrangement, comparison and explanation; but it has no pretensions whatever to represent the entire and absolute truth with regard to the constitution of bodies; it simply exhibits them from one of many excellent points of view; it has reference less to the actual constitution of the bodies than to our particular mode of regarding them.

In proportion to the complexity of the constitution of a body, so is the number of aspects in which it may be regarded, so is the number of rational theories that may be entertained concerning it. All of these theories belong to the same order of truth; they differ from one another only in their greater or less degree of generality. The theory of the greatest generality most nearly approximates to the representation of bodies, especially typical bodies, by empirical formulæ, as unitary molecules.

Adopting the proportional numbers of Gerhard, we represent the two-volume molecules of muriatic acid, water, ammonia, and coal-gas by ClH , OH^2 , NH^3 , CH^4 respectively. In accordance with certain theoretical notions, these bodies have been formulated as follows:—



Laurent.



Kane.



Liebig.



Wurtz.



Dumas.



Odling.



Coal-gas may be represented as terhydride of formyle, analogous to its derivative chloroform, or terchloride of formyle. The two bodies can be prepared in virtue of analogous equations from acetic and chloracetic acids respectively, and the one can be obtained from the other by direct substitution.

Each of the above theories has certain circumstances in its favour; each is true to a certain extent; each represents the body in question

from a different point of view ; sometimes one point of view is most advantageous, sometimes another. As a veritable representation of the constitution of coal-gas, Dumas' view is preferable to either of the other two theoretical views.

The adoption of Laurent's sarcastic suggestion of peroxide of hydrogen as a compound radical, leads to inadmissible or uncertain results; thus, Is potash oxide of zinc, KZO, a combination of a hypothetical peroxide of potassium with zinc, or of a hypothetical peroxide of zinc with potassium? Is Williamson's double æther, MeEtO, a combination of peroxide of methyle with æthyle, or of peroxide of æthyle with methyle, &c.?

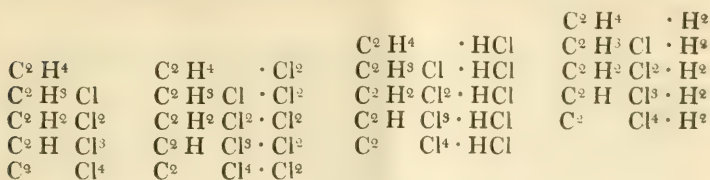
Nevertheless there are greater grounds for recognizing peroxide of hydrogen as a compound radical, than there are for recognizing æthyle and methyle as such. A large number of bodies may be represented very feasibly as containing æthyle; but an infinitely larger and more varied set of bodies may be represented as containing peroxide of hydrogen; such, for instance, are water, potash, sulphuric acid, formic acid, benzoic acid, hypochlorous acid, &c., and, as has been shown by Mr. Brodie, very many other more complicated bodies. Many equations may be represented very simply by means of æthyle analogous to hydrogen; but a much greater number may be represented by means of peroxide of hydrogen analogous to chlorine. Æthyle has been obtained in the free state, so has peroxide of hydrogen; but whereas nearly all the bodies of the peroxide of hydrogen series can be obtained directly from it, not one single æthylic combination has ever yet been obtained from æthyle. Hydrogen and æthyle present certain analogies, but the analogies of chlorine and peroxide of hydrogen are much more complete. Both bodies bleach, oxidize, combine directly with potassium, set free bromine and iodine, and take the place of the bromine and iodine set free. In $\text{Ba} \cdot \text{OH}$ and in BaCl the Ba can be readily detected; but with regard to HCl and EtCl , the Cl can be detected in the former only.

All the facts connected with the mutual relations of—

$\text{C}^2 \text{H}^4$	æthylene, or olefiant gas,
$\text{C}^2 \text{H}^4 \text{O}$	aldehyde,
$\text{C}^2 \text{H}^4 \text{O}^2$	acetic acid,
$\text{C}^2 \text{H}^6$	hydroæthylene,
$\text{C}^2 \text{H}^5 \text{Cl}$	muriatic æther,
$\text{C}^2 \text{H}^6 \text{O}$	alcohol,

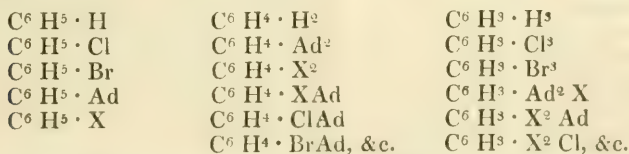
especially since the recent researches of Berthelot show the superiority of Dumas' æthylene to Liebig's æthyle theory, both as regards its more complete accordance with experiment and its greater generality. The probabilities in favour of the pre-existence of $\text{C}^2 \text{H}^4$ and its derivatives, as constituent groups, are much greater than are those in favour of the pre-existence of $\text{C}^2 \text{H}^5$. Thus, with regard to æthylene, hydroæthylene, muriatic æther, and their chlorine deriva-

tives, we ought to have the following series, convertible into one another through certain members:—



Of these four series, three are undoubtedly, and the fourth most probably, known to us. They illustrate rationally the nature of the isomerism. In the three latter series, we have every reason to believe, that, with regard to the carbon, two of the hydrogen or chlorine atoms stand in a different relation to the other four; but in the first series, we have not a single fact tending to show that one of the hydrogen atoms stands in a different relation to the other three; not one fact to countenance the representation of olefiant gas by $C^2 H^3 \cdot H$, hydruret of acetylene.

In the next best-known hydrocarbon, namely benzene, there is no more reason for believing in the existence of the monobasic radical phenyle, $C^6 H^5$, than there is for believing in the bibasic and tribasic radicals, $C^6 H^4$ and $C^6 H^3$ respectively, as seen in the following table ($X = NO^2$ Ad = NH^2):—



Lastly, Williamson's othyle theory, although it possesses a great degree of generality, and is supported by most complete analogies both in mineral and in organic chemistry, is only one of many ways of indicating the mutual relations of bodies. It must not be taken as the sole veritable representation of the constitution of the compounds to which it applies. There are no greater proofs of the pre-existence of othyle in acetic acid than there are of the pre-existence of peroxide of hydrogen in water.

For example, the correlations of benzamide, benzonitrile, hydrobenzamide, and dibenzoylimide are entirely neglected in the othyle theory. These bodies belong to one single class; they all contain certain benzoic elements and certain ammoniacal elements; by the absorption of water they yield ammonia and benzoic acid or aldehyde. But the othyle theory bears no reference to this point of view; it separates benzamide widely from its congeners. Thus we are told that the first body contains the compound radicals benzoyl (analogous to othyle) and amidogen; the second, the compound

radicals phenyle and cyanogen; the third, nitrogen and the compound radical benzyle (analogous to acetylene); whilst, with regard to the fourth, as to many other bodies, the compound radical theory fails altogether.

In the three best known hydrocarbons, coal gas, olefiant gas and benzine, as in many other bodies ordinarily represented as containing compound radicals, the conception of self-existent constituent compound radicals is not only unnecessary but irrational. The particular groupings of atoms, which we denominate compound radicals, do not have an existence apart from the other constituents of the bodies, into which they are said to enter.

PATENT.

Patent granted to J. R. Johnson, for Improvements in the Manufacture of Type.

In the manufacture of type and other raised surfaces for printing, it has been usual for the most part to employ compounds of lead and antimony as the metal for casting the same, and in some cases a small per-centage of tin has been added. Now the object of this invention is to obtain harder, tougher, and more enduring type and raised surfaces for printing, by employing tin (in large proportions) with antimony, and greatly to reduce, or wholly omit, the use of lead with such metals when making type and raised surfaces for printing, by which means the type produced is so hard, tough and enduring, as to allow of its being used as a punch on the ordinary type-metal now used. The proportions employed by the patentee are 75 parts of tin to 25 of antimony, but this may be to some extent varied. When lead is also used, it must not exceed 50 parts in 100 of the combined metals employed; for if the lead be employed in much larger quantity, the hardness and toughness of the alloy rapidly decreases, and the alloy then approaches the ordinary type-metal in its properties, notwithstanding the presence of a considerable quantity of tin.

The tin, or mixture of tin and lead, is first fused; and the scum or dross having been removed, the antimony is added, continuing the heat until combination takes place; the alloy is then again skimmed, and run into ingots for use.

When the antimony is tolerably pure, the best proportions are as given above, 1 part of antimony to 3 of tin, or tin and lead; but when it contains other metals, the quantity of antimony should be diminished, or, which is preferable, the metal should be repurified. If this be not attended to, the alloy, although of great hardness, does not possess the tenacity or toughness necessary for type of extreme durability.—Dated April 7, 1854.

THE CHEMICAL GAZETTE.

No. CCCII.—May 15, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of Flame. By Dr. W. HILGARD.

THE author has made a series of experiments on flame in Bunsen's laboratory, by the methods described by Bunsen in the 'Report of the British Association for 1845.' With Berzelius, he divides the luminous flame into four parts, namely, 1st, the blue zone below the flame; 2nd, the internal cone; 3rd, the luminous sheet; and 4th, the halo, or the external faintly luminous stratum surrounding the flame from the top to the bottom.

The gaseous products or contents of these portions of the flame, produced by a lamp specially adapted for this purpose, were drawn out of the flame by means of tubes immersed in the different parts of the flame, collected in receivers, and analysed. The results led to a conviction, that the chemical processes in action in the separate parts of the flame are by no means so simple as has generally been supposed from the older investigations, and are partly of a totally different nature.

The luminous flame is generally regarded as a medium offering a certain degree of resistance to the pressure of the air from below and from the sides. The author's experiments however show that this is not the case, but the air rather permeates the flame in certain directions, as is indicated by the amount of nitrogen. Thus below, where the wick of the lamp or candle limits the air drawn up by the flame, the air enters the flame in an almost horizontal direction, and the lower part of the flame, above the level of the wick, contains the greatest amount of nitrogen; the flame below the level of the wick, on the contrary, contains a smaller quantity of nitrogen, on account of the slow evolution of the gases, as these are evolved at some distance from the source of heat, and consequently at a lower temperature. In the lamp adopted by the author, it appeared that there was a point in the inner cone of the flame, up to which, from the level of the wick, the amount of nitrogen gradually increased; above this point it decreased up to a second point, after which it constantly increased to the apex. In the interior of the flame, processes of oxidation and reduction take place simultaneously with those of dry distillation, in a manner that can be imitated by no apparatus contained in our laboratories; the oxygen constantly streaming in from the exterior with the air, furnishes a mixture of gases with the products of the dry distillation, and this passes through a series of tempera-

Chem. Gaz. 1855.

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tures, each of which produces its peculiar effect. In this mixture, carbonic acid, vapour of water, and free oxygen are present as oxidizing agents; carbonic oxide, hydrogen, hydrocarbons, and free carbon as reducing agents. The greatest amount of permanent gases is formed at the apex of the flame, where the heat is sufficient suddenly to decompose the condensible matters suspended in the interior, by which more considerable quantities of permanent gases are formed than in the deeper parts of the flame, and the greater evolution of gas in this upper portion is also indicated by its form.

The quantity of carbonic acid, and also more or less that of the carbonic oxide gas, is proportionate to the amount of nitrogen, as it arises from the oxygen which accompanies the latter. The carburetted hydrogen and hydrogen gases exhibit no remarkable, or at all events no corresponding changes in regard to the region of strong evolution of gas; with tallow, elayle gas and light carburetted hydrogen appear to increase in quantity, whilst carbonic acid, carbonic oxide, and hydrogen decrease. With regard to the separate portions of the flame, the author makes the following statements at the conclusion of his memoir:—

1. Regarding the *blue zone at the base of the flame*, the author confirms Plattner's opinion, that it consists of the carbonic oxide formed by the first and weakest action of the heat, with a little carburetted hydrogen. Volger's arguments against this view are incorrect. Plattner also stated, that the blue cone of the blowpipe-flame is identical with this zone. This opinion has been disputed by Volger upon erroneous grounds, as shown by the author, who proves the correctness of Plattner's views, but endeavours to find the origin of the luminosity and non-luminosity of flames in other conditions.

Thus, according to the author, it is unnecessary to suppose a chemical peculiarity in the inner cone and this blue zone, to account for non-luminosity. Davy already recognized two circumstances as the causes of the luminous power of a flame,—on the one hand a *diminution of temperature*, and on the other a dilution of the luminous gas by another which is less luminous during combustion. There are however in this case two very different influences to be distinguished. A gas which burns in the air with separation of carbon, will part with this carbon whether the external air be cold or hot; the difference will lie principally in the temperature to which the separated carbon is heated in the flame. A flame cooled from the exterior will diminish in size and become less luminous, in proportion as from its comparatively low temperature a portion of the carbon is enabled to escape without combustion. The other, and indeed the principal cause of diminished luminosity, is the complete suppression of the separation of carbon, and this takes place as soon as sufficient oxygen can have access to oxidize immediately both hydrogen and carbon; for instance, in the eudiometer, where, for example, elayle gas with a great excess of oxygen burns without any considerable evolution of light,—or in a flame burning in the open air, which is surrounded by a sufficiency of oxygen for its complete oxidation.

The blue zone at the base of the flame is therefore the consequence of the access of the oxygen of the air, not, as in the upper part of the flame, in a rarefied state, but, as in the blue cone of the blowpipe-flame, unrarefied, and consequently in excess. The blue zone disappears on the upper part of the flame, because here, from the conical form of the flame, the current of air, which from its greater rarefaction is directed more upwards, no longer falls upon the surface of the flame in a nearly perpendicular direction, but only touches upon it. Hence also the carbonic oxide gas, which is very strongly heated towards the upper part of the flame, no longer burns with a blue flame, but with a scarcely visible yellowish-red flame.

2. *The inner cone of the flame* constitutes the apparatus for the gasification of the products of distillation, which rise from the combustible material of the wick. With these products mingle the products of oxidation of the burning sheet, which is permeated by the surrounding atmosphere, namely, vapour of water and the oxides of carbon, together with the nitrogen of the air, which remains after the disappearance of the oxygen. In consequence of this admixture, the proportions of the gases in the inner cone must vary at different heights, although the processes which here take place can only vary in degree, and not in their nature.

3. *The luminous sheet* is the true apparatus of combustion in the flame, and from it the luminous effect is produced. Its outer surface contains oxygen from the surrounding, its inner combustible gases from the internal cone. As the free oxygen of the air must pass through a considerable space during its combustion in the luminous sheet before it reaches the inner cone in the form of aqueous vapour and oxides of carbon, it must be constantly diminishing during this progress, and the vividness of the combustion must diminish in the same proportion. Hence the darker colour of the upper and inner portion of the luminous sheet, which has induced Waldie and Volger to regard this as a separate portion of the flame. The form of the luminous sheet is also readily and simply explicable from these processes. All the upper parts of the flame receive from those lying below them the products of the combustion there taking place, and these mingle with the gases produced on the spot. From this circumstance, and the constant consumption of the products of distillation of the inner cone, the flame is constantly getting poorer in combustible materials as we approach its apex. The air which penetrates the upper parts of the flame, in consequence of this constant diminution of the oxidizable matters, will have always to pass through a constantly increasing space before the free oxygen entirely disappears; the thickness of the luminous sheet must therefore increase towards the apex of the flame, and this is the reason why the luminous sheet appears to be a hollow cone below and a solid one above. It is almost exclusively in this luminous sheet that the separation of carbon, caused by the decomposition of the elayle, takes place; the ignition of this is the cause of the luminosity, and the true reduction-space of the flame therefore lies in the border of the luminous apex of the flame, which is

turned towards the inner cone, whilst the reducing action must gradually diminish towards the opposite border in proportion as the quantity of free oxygen for the combustion of the free carbon increases. This also applies to the oxidizing and reducing spaces of the blowpipe-flame.

4. *The halo of the flame.*—The halo surrounds the whole of the flame. Volger's statement, that it only envelopes the lower part of the flame, is founded in error; this may easily be seen by holding a model of the flame in front of it, so as to get rid of its dazzling effect, or, what is better, by putting a little phosphoric acid or some soda-salt upon the wick, when the halo is rendered visible to the naked eye. It only becomes a little thinner at the base, and is thicker at the apex of the flame than at the sides. As regards its chemical nature, it consists of incandescent atmospheric air, mixed with the final products of combustion; it has the colour of slightly incandescent nitrogen.

With regard to the temperatures of the different parts of the flame, the author indicates the great uncertainty of the methods which have been employed in their determination. The methods adopted by Davy, Sym, Murray, Porret, and Becquerel are not sufficient for the purpose; the author therefore proposed to calculate, from the known composition of the gases of flame, the amount of heat which will be set free during the combustion of the combustible constituents, and arrived at the conclusion, that no certain result can be obtained in this manner, as the gases of the flame do not mingle uniformly with the air, and the heat of the lower parts is communicated to those above them.

With regard to the strength of light given by equal wax and tallow flames, which according to Peclet are as 13·6 : 7·5, the wax flame being whiter, more slender, and less bulging at a certain part than that of tallow, which burns dingily and smokes readily, the author remarks that this distinction lies not only in the elementary composition, but especially in the unequal supply and decomposition of the combustible materials. The proportion of oxygen is different in each flame; when the access of oxygen is scanty, carbon of course separates from every flame containing that body, whilst with an excess of oxygen the richest flame in carbon must become converted into a blue blowpipe-flame. The analysis of the gases distinctly indicates the difference in the elementary composition. The great amount of carbonic acid in the lower, and its rapid increase in the upper parts of the *tallow flame*, therefore, arise from the circumstance, that the original amount of oxygen contained in this combustible material is nearly twice as large as in wax. But nearly the same proportion occurs in stearic acid, the flame of which scarcely yields to that of wax in strength. The cause of the difference therefore lies in the amount of oleic acid in the tallow, and this requires two things to be taken into consideration, viz. the excessive supply of melted combustible matter on account of the low melting-point, and its more ready decomposability. The author found that the formation of elayle gas takes place much higher in the wax flame

than in tallow, so that in the tallow flame the decomposition of the elayle commences at a much lower point in the flame; the quantity of elayle then diminishes rapidly, and to judge from the large quantity of carburetted hydrogen, more so than with wax, by mere heat and without simultaneous oxidation. The author however leaves the cause of the greater weakness in the light of the tallow flame undetermined. According to his experiments, the remarkable phenomenon occurs, that tallow gas contains 19 per cent. of elayle, and wax gas only 15 per cent. The two flames were however produced under very slightly varying circumstances, and one might consequently have supposed that the former, as it contained more luminous gas, should have been the brighter.

With other combustible materials the flame is variously modified. The luminous part is frequently suppressed, the halo more rarely; the blue zone, being the part where the undiluted combustible gas is in contact with fully oxygenated air at a low temperature, is almost always present.

In the *alcohol flame* the four parts exist. The inner cone is very large, in consequence of the volatility of the combustible material; the luminous sheet, from the very small separation of carbon, forms a very thin conical coat; and the halo appears very large, in consequence of the slight luminosity of the flame.

The flame of *carbonic oxide gas* has a distinct dark cone; the halo is yellowish-red, and not distinctly separated from the atmosphere, the lower zone is dark blue.

The flame of *sulphur* has a blue zone, and the halo is reddish-violet.—Liebig's *Annalen*, xcii. p. 129.

On Lithium and Strontium. By M. BUNSEN.
(Extract of a Letter to M. Regnault.)

I send you a small specimen of lithium, which I have prepared in concert with Mr. Matthiessen by electrolysis. It forms a wire of several decimetres in length, and about three-fourths of a millimetre in diameter.

Lithium has the colour and brilliancy of silver, from which it would be impossible to distinguish it by its appearance; but it is so readily oxidizable, that the contact of the air blackens it immediately. It must be preserved in naphtha and in tubes deprived of air. Its ductility is so great, that I was able to draw out a small fragment weighing 5 milligrms. into a wire of several feet in length. It melts at 356° F., and is the lightest of all known solid or liquid bodies; its density does not exceed 0.5936. It burns with great brilliancy and a white light in oxygen, chlorine, and vapours of bromine, iodine and sulphur. It decomposes cold water immediately, with a brisk effervescence.

I also send a specimen of strontium, prepared in the same way by Mr. Matthiessen. The metal is in the form of a brilliant plate, of a bright brassy-yellow colour. On touch-stone it leaves a brilliant line of a golden-yellow colour, which however almost instantly be-

comes of a copper-red, in consequence of superficial oxidation. This metal decomposes water very quickly, even in the cold; it burns with a very brilliant white light in oxygen, chlorine, bromine, iodine and sulphur. Placed in a voltaic circuit with calcium and water, it proved to be negative with regard to the latter metal, which is a very singular fact. Strontium is a very ductile metal; its density is 2.542, whilst that of calcium is only 1.584.—*Comptes Rendus*, April 2, 1855, p. 717.

On the White Colour of the Iron Alums, and the Brown Tint of their Aqueous Solutions. By H. ROSE.

The author shows, that during the solution of white iron alum, the water extracts acid from the peroxide of iron, and forms a basic persalt of iron, which is soluble in a large quantity of water at ordinary temperatures, or in a small quantity at an elevated temperature; the oxide is however precipitated as a basic salt from the dilute solutions when heated. All the basic persalts of iron, however, whether in the solid form or in solution, are coloured either yellow, brownish-red or blood-red; hence the colouring of the watery solution of the white salt. If the white salt be dissolved in dilute sulphuric acid, no basic salt can be formed, and the solution consequently remains colourless.—*Bericht der Akad. der Wiss. zu Berlin*, 1855, p. 85.

On the Decomposition of Sulphate of Baryta by means of Alkaline Carbonates. By H. ROSE.

The author states that sulphate of baryta is scarcely, if at all, decomposed by solutions of alkaline carbonates at ordinary temperatures, and that an extremely trifling decomposition only takes place after long standing, especially during the summer. Solutions of alkaline bicarbonates behave in the same manner. When boiled, as is well known, decomposition is effected; but the author contradicts the general opinion, that sulphate of baryta cannot be entirely decomposed in the humid way by the employment of any quantity of alkaline carbonate, although he shows that the amount of the latter must be very considerable to effect this, as it requires no less than 15 atoms of either of the alkaline carbonates to decompose 1 atom of sulphate of baryta. If 1 equiv. of sulphate of baryta be boiled with 1 equiv. of a solution of an alkaline carbonate, only about one-ninth or one-eleventh of it will be decomposed, according as carbonate of potash or soda is employed. It is the presence of the alkaline sulphate formed that impedes the decomposition of sulphate of baryta by an alkaline carbonate.

If sulphate of baryta has been boiled with the alkaline solution, the fluid poured away from the residue, and the latter again treated with a solution of the alkaline carbonate, complete decomposition takes place, particularly when the operation has been twice repeated. When sulphate of baryta is boiled with a solution of an alkaline

carbonate and sulphate, containing equal weights of both salts, it remains unchanged. The author shows by experiments that in this case other affinities, besides that of the sulphate of baryta, to the alkaline sulphate are in action, especially that of the alkaline sulphate to the carbonate, that of the carbonate of baryta to the alkaline carbonate, and even to the sulphate of baryta; and, lastly, the influence of the water, which has a decomposing action upon the corresponding double compounds.

On the other hand, carbonate of baryta is converted by a solution of an alkaline sulphate into sulphate of baryta, even at ordinary temperatures. If sulphate of baryta be melted with an alkaline carbonate, and the melted mass treated with water, the complete decomposition of the sulphate of baryta may be effected with a smaller quantity of the alkaline carbonate than in the humid way. It then requires only 6 or 7 equivs. of carbonate of potash, and 8 or 9 equivs. of carbonate of soda.

Sulphate of baryta is not decomposed by a solution of carbonate of ammonia, either at ordinary or at elevated temperatures. Carbonate of baryta is not converted into sulphate when treated with a solution of sulphate of ammonia at the ordinary temperature, but this decomposition takes place very readily by boiling. The author also shows that sulphate of baryta does not always exhibit the perfect insolubility in dilute acids which is generally attributed to it.—*Bericht der Akad. der Wiss. zu Berlin*, 1855, p. 98.

Upon some Oils of the Dolphin, and on Phocenic Acid.
By M. BERTHELOT.

Since the discovery of valerianic acid, it has been supposed that the volatile acid of the fat of the dolphin, to which Chevreul first gave the name of phocenic acid, is valerianic acid. Probable as this identity appeared, however, it was doubted by some chemists. But Heintz's work upon the fats must especially be regarded as contradicting this identity, as Heintz found that the neutral fats of the animal kingdom only contained numbers of atoms of carbon divisible by four. Berthelot has therefore examined the fat of several dolphins, and amongst others that of *Delphinus marginatus*, Cuv., and also that of some sharks, such as *Mustelus vulgaris*, Cuv., and *Scymnus niceensis*, Cuv., and always found that the volatile acid was valerianic acid. To ascertain the presence of volatile acids in fat, Berthelot distils at a gentle heat 100 grms. of the fat with 100 grms. of a mixture of alcohol and sulphuric acid. If the first portion of the distillate be mixed with water, the æthers of the volatile acids separate.

The author afterwards prepared valerianic acid in the ordinary manner, and analysed it and its æther. The results obtained were distinctly in favour of the identity of the so-called phocenic acid with valerianic acid.—*Journ. de Pharm. et de Chim.*, 3 ser., xxvii. p. 35.

On Bimucate of Oxide of Amyle. By S. W. JOHNSON.

In the year 1836, Malaguti described the neutral compounds of mucic acid with the oxides of methyle and æthyle. The author has prepared and investigated the compounds of mucic acid with oxide of amylen.

If fuming muriatic acid be added to a mixture of mucic acid, English sulphuric acid and amylic alcohol, and the mixture be digested for some hours, *bimucate of oxide of amylen* = $C^{10}H^{11}O$, $HO + C^{12}H^8O^{14}$, is obtained. A semi-solid brown mass is first formed; this is washed with alcohol, and then recrystallized from water or alcohol. When the solutions are not too much concentrated, the æther is obtained in colourless crystals. It is readily soluble in hot water and alcohol; when dry, it is fatty to the touch, and is scarcely moistened by water. It gives an acid reaction with moist litmus.

The solution is not precipitated by salts of baryta and silver, or by ammonia. The alkalies, potash, soda, and ammonia set free oxide of amylen. The boiling watery solution has a slight odour of fusel-oil, in consequence of a gradual decomposition. It does not expel carbonic acid from the weakest combinations.

It is worthy of remark, that the acid æther of the amylen series is readily produced, whilst the neutral æther could not be prepared; and in the æthyle series the neutral æther is readily obtained, but the acid one is formed with difficulty. The analysis of the æther is as follows:—

Carbon.....	46.99	46.69	22 =	132	47.14
Hydrogen	7.08	7.29	22	20	7.14
Oxygen	45.93	46.02	16	128	45.93

Journ. für Prakt. Chem., lxiv. p. 157.

ANALYTICAL CHEMISTRY.

On the Employment of Chloride of Silver in Qualitative Analysis with the Blowpipe. By H. GERICKE.

AMONGST the phænomena which characterize different bodies before the blowpipe, and serve for their distinction, the colour of the flame is of no small importance. This power of colouring the blowpipe-flame is not however exhibited by all bodies with sufficient intensity to enable them to be distinguished by it with certainty; and certain substances are consequently usually employed, such as muriatic acid with baryta, strontian and lime, or sulphuric acid, partly to form and partly to set free volatile compounds. By this means, however, although the intensity of the coloration is heightened, its duration is not increased, as these acids, and particularly muriatic acid, evaporate for the most part before they have acted sufficiently, so that the coloration lasts only for a few moments. This defect may be

got over by the employment, instead of the volatile muriatic acid, of a chloride, which will retain the chlorine at a high temperature, so that it may only be set free by degrees in small quantities, whilst the body forming its base may be without action upon the colouring power of the body under investigation. For this purpose chloride of silver appears to be the best, especially as it may readily be prepared in a state of purity. The best plan is to stir it with water into a thick paste, and keep it in a bottle.

In regard to the action of chloride of silver upon the coloration of the blowpipe-flame, I have investigated several compounds of potash, soda, lithium, lime, baryta, strontian, copper, molybdenum, arsenic, antimony and lead, and mixtures of these substances. Chloride of silver, of course, has no action upon borates and phosphates, both these acids being amongst those which offer the most resistance to the action of heat.

For a support I employed first of all platinum wire, but this is soon alloyed by the metallic silver which separates, and thus soon rendered useless in testing metals. Silver wire is too readily fusible, and also difficult to obtain free from copper, which may give rise to errors when in contact with the chloride of silver. For these reasons iron wire is best fitted for experiments with chloride of silver, as from its cheapness a new piece may be employed for each experiment, whilst the silver may be readily obtained in the form of chloride from the broken pieces. If the size of the fragment under examination be sufficient, the platinum forceps may be employed.

The results at which I have arrived by the employment of chloride of silver, in comparison with those obtained without this reagent, are as follows:—

With potash compounds, such as saltpetre, potashes, &c., the flame is decidedly of a darker colour with chloride of silver, and even with ferrocyanide of potassium, which, when treated by itself with the blowpipe, colours the flame blue; the addition of chloride of silver produces a distinct potash coloration.

The action of chloride of silver upon soda salts is not so favourable; for although with some, such as nitrate of soda, common soda and labradorite, the flame acquires a more intense yellow colour by the addition of chloride of silver, this reagent produces no observable difference with other soda compounds, such as sulphate of soda and analcime.

This also applies to the compounds of lithia, some of which give a finer purple-red colour on the addition of chloride of silver, whilst upon others it has no such effect.

With lime compounds chloride of silver acts favourably upon the colouring power. Thus the addition of chloride of silver to calcareous spar or gypsum (in the reduction-flame) gives the flame a more distinct yellowish-red colour; but stilbite gives no lime coloration either with or without chloride of silver. With fluor-spar the coloration cannot well be observed, as this decrepitates too violently under the blowpipe.

The action of chloride of silver upon compounds of baryta and

strontian is decidedly advantageous, as both the intensity of the coloration and its duration leave nothing to be desired. Sicilian cœlestine, which when heated by itself in the forceps scarcely coloured the flame, immediately produced a permanent red coloration when heated with chloride of silver.

Although it appears from the preceding statements that the employment of chloride of silver presents no advantage with some substances, it may be used with good results in the treatment of mixtures of alkalies and earths.

Thus with *petalite* alone the lithia coloration is first produced, and a slight soda coloration is afterwards obtained, whilst with chloride of silver the soda coloration appears very distinctly after that of the lithia. With *lithion-mica* alone a very distinct lithia coloration is presented; but in the presence of chloride of silver a colour is first produced, which may lead to the conclusion that potash is present, but the lithia coloration is weakened. *Ryacolite*, heated by itself in the blowpipe-flame, only gives a distinct soda coloration; but with chloride of silver a slight potash coloration is first produced, and the colour of soda then appears very distinctly; the lime contained in it cannot however be detected by the coloration of the flame.

But chloride of silver may be employed with still greater advantage with the following metals; but in these cases it is particularly necessary that the operator should become familiar with the colour produced by each individual substance.

With copper compounds, such as red copper ore, malachite, copper pyrites, sulphate of copper, &c., when contained in other minerals so as to be unrecognizable by the eye, the employment of chloride of silver may be of the greatest service, as the smallest quantities of copper, when treated with chloride of silver under the blowpipe, give a continuous and beautiful blue colour to the flame. With chloride of silver the presence of copper may be distinctly ascertained by the blowpipe, even in a solution which is no longer coloured blue by the addition of ammonia.

The employment of chloride of silver will be equally advantageous with molybdenum, as in this case also the flame gains greatly in intensity. Arsenic, lead, and antimony are already sufficiently characterized, the former by its odour, the two latter by their fumes; but even with these metals chloride of silver may be employed with advantage, to render their reactions still more distinct. It is only necessary to observe that the greenish blue flame of antimony appears greener and more like that of molybdenum under the influence of chloride of silver.

Chloride of silver may also be employed with compounds containing several of the above-mentioned metals. If *bouronite* be heated in the oxidation-flame of the blowpipe, a fine blue flame is first produced, which indicates lead with certainty; if chloride of silver be now applied, copper is also readily shown. The antimony contained in *bouronite* cannot be ascertained by the coloration of the flame; but this may be easily detected upon charcoal or in a

glass tube open at both ends. Native molybdate of lead without chloride of silver only gives a blue colour to the blowpipe-flame; with chloride of silver this blue coloration of the lead comes out more distinctly, but at the same time the tip of the flame, particularly when the reduction-flame is employed, appears of a beautiful yellowish-green colour from molybdenum. With mixtures of arsenic and copper, or antimony and copper, the flame first acquires a grayish-blue or greenish-blue colour from the oxidation of the arsenic or antimony; the copper may then be very easily detected by chloride of silver. This applies also to mixtures of arsenic and molybdenum, or antimony and molybdenum; with chloride of silver the yellowish-green flame of molybdenum appears distinctly. It will be more difficult to analyse mixtures of arsenic and lead, or antimony and lead, in this manner; and if a compound contain both arsenic and antimony, these two bodies are not to be distinguished with chloride of silver under the blowpipe.

From these experiments it appears that in blowpipe-testing it is more advantageous to employ chloride of silver, instead of muriatic acid. Chloride of silver is particularly to be recommended in testing metallic alloys for copper. Thus to test silver for copper, chloride of silver may be applied to the ends of silver wires, and on the application of heat the smallest quantity of copper will furnish the most distinct reaction. This is as sensitive as any of the known copper reactions, and may be performed quickly and easily. In testing metallic alloys for traces of copper, it may be advisable to submit those which contain antimony, zinc, lead, and other volatile metals, to roasting, so as to drive off these metals before the addition of the chloride of silver.—*Chem. Pharm. Centralblatt*, March 27, 1855, p. 195.

On the Volumetric Determination of Iron. By Dr. A. STRENG.

In a recent number of the 'Annalen der Chemie und Pharmacie,' there is an article by Dr. Mohr, in which my paper "On a Method of Volumetric Analysis of general application*," is adverted to. He also mentions a point, which I have long proposed to work out, namely, the peculiar behaviour of the oxides of iron towards the reagents recommended by me, and the volumetric determination of those compounds. Mohr observed this behaviour when attempting the determination of oxide of manganese by my method, which did not succeed, from the oxide of manganese containing, as is almost always the case, peroxide of iron.

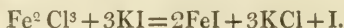
If an acid solution of chloride of tin be added to an oxide of manganese of this description, not only is the peroxide of manganese reduced to the state of protoxide, but the peroxide of iron also ($\text{Fe}^2\text{O}_3 + \text{SnO} = 2\text{FeO} + \text{SnO}^2$); and it is consequently impossible, from the amount of chloride of tin employed, to arrive at any conclusion as to the quantity of peroxide of manganese contained in the mineral. Mohr also observed, that a solution of chloride of iron

* *Chem. Gaz.*, 1854, p. 250.

behaved towards iodide of starch quite differently from chloride of tin; the latter decolorizes the blue compound, the former does not do so. Bichromate of potash may therefore be employed for the oxidation of protochloride of iron, as proposed by Schabus and Penny; but the completion of the reaction cannot be recognized by the addition of iodide of potassium and solution of starch, as the first drop of the chromic solution causes a separation of iodine and a formation of the blue compound.

As therefore, on the one hand, peroxide of iron is reduced by chloride of tin, and on the other protoxide of iron is not oxidized by periodide, a simple determination, similar to that of tin, is certainly not possible, but a determination of iron might perhaps be effected by converting this body into peroxide, reducing the peroxide to protoxide by chloride of tin, and ascertaining the excess of chloride of tin by means of a standard solution of chrome. I therefore repeatedly endeavoured to extend the application of my method to iron, in the hope of rendering it possible to make an analysis of native oxide of manganese by a separate determination of the iron, but I could arrive at no correct results; and although I employed all possible care, I always obtained too little iron. I was compelled therefore to give up this determination of iron, but will still continue my experiments, so as at all events to discover the cause of this remarkable phenomenon.

As my endeavours to arrive at a result in this way failed, it only remained for me to fall back upon the older method of Duflos, for the determination of iron. This method is founded upon the following reaction:—



If therefore an excess of iodide of potassium be added to a solution of peroxide of iron, a separation of iodine takes place, 1 atom of iodine being set free for every 2 atoms of iron. Duflos determines this free iodine by means of a standard solution of chloride of tin, which is to be added until the brown colour of the iodine has entirely disappeared and the fluid has become perfectly colourless. As however a solution of chloride of tin is constantly changing its composition, it is necessary to test its strength frequently; this is best effected by means of a standard solution of bichromate of potash, as described in my previous memoir.

The recognition of the completion of the reaction is not quite certain by Duflos's method, as the colour of the solution of iodine becomes very pale towards the end. In this case also a clear solution of starch may be added towards the end of the reaction, whilst the colour of the iodine is still distinctly recognizable; this produces an intense blue colour. If the tin solution be still dropped in, a point is arrived at when the iodide of starch is suddenly decolorized.

The following is the process for combining Duflos's method with mine. The substance containing iron is dissolved in muriatic acid; and in case it might contain protoxide of iron, it is boiled with a few granules of chlorate of potash until the odour of chlorine has

entirely disappeared. The solution is then diluted with cold water, an excess of a solution of iodide of potassium is added to it, and a dilute solution of chloride of tin, the strength of which has previously been determined by means of a standard solution of bichromate of potash, is poured in from a burette. The iron solution, which is coloured brown by the free iodine, becomes constantly paler during the addition of the chloride of tin. When only a small quantity of free iodine is still contained in the solution, a clear solution of starch is added, and the addition of the chloride of tin is carried on with more care, stirring the mixture after the fall of each drop. As soon as decoloration has taken place, the addition of the tin solution is stopped. That this point really indicates the completion of the reaction is shown by the fact, that one or two drops of a solution of chrome are sufficient to reproduce the blue tint of the iodide of starch. The experiment might therefore be varied by adding the tin solution without any addition of starch until complete decoloration, and then adding solution of starch, so as to ascertain the small excess of the tin solution by means of the standard solution of bichromate of potash. The first-described method is however shorter, and therefore to be preferred.

It is remarkable, moreover, that this analysis is excellent in the presence of a sufficient quantity of iodide of potassium; whilst if only a small quantity of this body is present, the production of iodide of starch does not indicate the completion of the reaction. This may perhaps be explained in this manner, that with an excess of iodide of potassium the analysis depends upon a simple determination of iodine, and that this is not injured by the presence of iron.

For the calculation of the analysis, the normal solution of chrome may be prepared as recommended by Mohr, so that 1 litre of it may contain one-thirtieth of an equivalent, or 4.957 grs. of K.O. 2CrO_3 . But I have hitherto preferred making use of the formulæ, because a normalization of the solutions according to a rational principle would be of little use here, the tin solution being constantly subject to change. I can scarcely believe indeed that it will remain unaltered when preserved, as recommended by Mohr, in an atmosphere of carbonic acid gas, which must be renewed after each employment of it, as it would be very difficult to prevent the access of atmospheric air. It is consequently impossible to determine the percentage contents of a substance by simple subtraction of the degrees of the burette; a multiplication and a subtraction will always be necessary. The formulæ proposed by me have a complicated appearance, but they consist for the most part of constant numbers, which may easily be calculated beforehand. I will therefore retain these formulæ for the present.

The per-centage amount of metallic iron is obtained from the following formula,—

$$x = \frac{100 \cdot \text{Fe c}}{\text{A} \cdot \text{K.O. 2CrO}_3} \cdot \frac{\text{CG}}{\text{g}}$$

in which c represents the value of 1 cub. centim. of the chrome

solution, G the number of cubic centimetres of the tin solution added to produce decolorization, g the number of cubic centimetres of the tin solution employed in testing its amount of tin, C the number of cubic centimetres of the chrome solution required for the oxidation of g, and A the substance employed.

If we calculate the known factors in the equation, it receives the following form :—

$$x = \frac{113.05}{A} \cdot \frac{cCG}{g}.$$

To simplify the subsequent calculation, the chrome solution may be normalized in such a manner that $c=0.01$ gr., and exactly 1.1305 gr. of the substance to be examined for iron may be weighed off, so as to obtain the formula,—

$$x = \frac{CG}{g},$$

the simplest expression for arriving at the per-centage amount of metallic iron. All the formulæ proposed in my previous memoir may also be readily simplified in the same manner.

To test the method, fine pianoforte wire was analysed in the manner above described :—

I.		II.	
A =	0.2 gr. iron wire		0.2 gr.
G =	10.0 cub. centims.		9.85 cub. centims.
g =	11.6 ...	11.25	...
C =	20.55 ...	20.0	...
c =	0.01 ...	0.01	...

Found.

0.2002 grm. Fe

0.19904 grm. Fe.

If the quantity of protoxide or peroxide of iron in any substance is to be found, the above formula requires alteration; instead of the equivalent of iron, that of the protoxide or peroxide must be introduced.

If the substance under investigation contain both protoxide and peroxide of iron, and this can be detected by muriatic acid, the amount of both may easily be found by testing two portions. One portion is dissolved in muriatic acid without access of air, mixed with an excess of iodide of potassium, and treated as above described; the amount of iron present as peroxide is calculated from this. The other portion is dissolved in muriatic acid, oxidized by chlorate of potash, and boiled until the entire disappearance of the odour of chlorine; by this the entire amount of iron is ascertained, so that the quantity in the form of protoxide may easily be obtained by deducting the result of the first analysis from that of the second.

I should have proposed the analysis of native oxide of manganese by this method :—Taking two portions; digesting the one with a known quantity of chloride of tin and muriatic acid, adding an ex-

cess of iodide of potassium, and determining by means of bichromate of potash the amount of oxygen furnished by the peroxides of iron and manganese to the chloride of tin; and boiling the other with muriatic acid alone until it is completely dissolved, and after the addition of a large quantity of iodide of potassium, determining the peroxide of iron only, so as to ascertain from both data the quantity of peroxide of manganese in the mineral; but I feared that this would be too tedious for technical purposes, particularly as Bunsen's test, or the chlorometric method proposed by Mohr, may readily be employed in this case.

I will take this opportunity to remark, that in my previous memoir I omitted to mention that the conversion of protoxide of manganese into peroxide by means of solution of chloride of lime must not be performed in an alkaline fluid, but in one slightly acidulated with acetic acid; if this be neglected, a solution of a permanganate is always obtained together with the peroxide of manganese, and the result will be falsified.—Poggendorff's *Annalen*, xciv. p. 493.

PROCEEDINGS OF SOCIETIES.

Royal Society.

March 29, 1855. (Thomas Bell, Esq., V.P., in the Chair.)

“On the Metallic and some other Oxides, in relation to Catalytic Phænomena.” By the Rev. J. Eyre Ashby.

I purpose to detail some experiments on the metallic (and a few other) oxides, made with a view to ascertain their powers to produce and maintain, catalytically, the combustion of various gases and vapours; and to annex such considerations as appear to be suggested by the facts. By catalysis I understand the operation of one body upon another, under favourable circumstances, whereby the second body is resolved into new chemical combinations, while the first (whatever may happen during the process) remains finally unchanged. This must be taken as not including explosion by percussion, in which the change takes place owing to the external application of dynamic force.

The apparatus for experimenting comprehends a variety of shallow capsules; wire-gauze, of iron, copper, and brass, of different degrees of fineness, cut into discs a little larger than the vessels on which they are to be superimposed; a spirit-lamp with large wick; a pair of pliers, and a few rings of wire to support the gauze, if necessary, while heating it in the spirit flame. The method of procedure is simple: the watch-glass, or capsule, is *nearly* filled with the liquid whose vapour is to be tried; on a wire-gauze disc is spread the oxide whose powers as a catalyser are to be tested, and this being warmed (more or less) over the lamp, is set down upon the upper rim of the capsule. Sometimes it is necessary to heat a

layer of the oxide in the middle of a small combustion-tube, and pass over it the gas, or mixture of gases.

I tried the following substances with pyroxylic spirit (hydrated oxide of methyle) and alcohol separately.

1. CoO appeared to possess the power in some degree, but perhaps the specimen was in too dense agglomeration, which is not essentially reduced by trituration.

2. Co_2O_3 maintained the catalytic combustion very well.

3. AgO , reduced to metallic silver, which shows a strong tendency on gauze, and acts perfectly in the combustion-tube.

4. U_2O_3 , HO became, at red heat, anhydrous mixture of UO and U_3O_4 , showing strong tendency. A very pure specimen catalysed the vapour as it changed from yellow to green, after which it died away. Will not act below 570° (F.).

5. SnO ; strong tendency.

6. SnO_2 ; slight tendency.

7. WO_3 apparently produces the effect if placed while glowing, over alcohol, but gradually dies away, as if very slowly cooling.

8. Pb_3O_4 changed to PbO , and showed a strong tendency, but quickly faded and grew cold.

9. CdO , placed while very warm over pyroxylic spirit, burst into glow and catalysed, but always died off after the lapse of from half a minute to two or three minutes, and then became incapable.

10. CaO (on the gauze), no effect.

11. SiO_2 exhibited a tendency.

12. Stourbridge clay; no effect.

13. Al_2O_3 appeared to have no effect in maintaining catalytic combustion on the gauze, but when made red-hot and quenched in absolute alcohol, it changed from pure white to a black substance and oxidized a portion of the alcohol. That this is not owing to carbon in the alcohol is evident, because the same change occurs when it is quenched in strong liquid ammonia. I suspect that it is a new oxide of aluminum.

14. Ni_2O_3 , formed by heating carbonate of nickel nearly to redness, failed; prepared from the common nitrate, it acted for a short time; reduced as an intensely black velvety substance from the purest nitrate, then warmed but not made red-hot, it glowed and catalysed with alcohol or ether. With pyroxylic spirit, it was left at the end of the operation of a greenish drab, which I suspect to be a mixture of Ni_2O_3 with NiO , although it may be Ni_2O_3 changed only in appearance, for when treated with nitric acid no nickel is dissolved.

15. MnO_2 is changed at red heat into Mn_2O_3 , which, with alcohol, ether, and pyroxylic spirit, continues the slow combustion very steadily. A specimen of very pure Mn_2O_3 acted extremely well, as did also a portion of "euchrome" (a hydrated sesquioxide of manganese (impure) dug from the estate of Lord Audley), after being heated in the air to drive away the carbonaceous matter with which it was mingled. Mn_2O_3 will, if sufficient care be taken, catalyse the moist gas arising from a strong solution of ammonia.

16. Fe_2O_3 , when in the state of a light puffy powder, catalyses the

vapour of ether, alcohol, and pyroxylic spirit, only requiring to be heated on the gauze before it is laid over the capsule. It is cheap, easily employed, and of invariable action. I have kept up the combustion for several hours on a surface of 120 square inches.

By means of a catalytic lamp in which the liquid employed is continually supplied from a reservoir and maintained at a constant level in the capsule, I have used 7 or 8 square inches continuously during thirty-six hours. This lamp I have occasionally used for laboratory purposes, where a gentle and equable heat was required for several hours.

Pursuing my experiments with the oxides of the metals, heated on wire gauze, I tried as many as I could procure or make, and by a tolerably wide induction I found that the *sesquioxides* have the strongest tendency to produce and maintain the catalytic glow, and do produce it in every case in which they are not decomposed by the amount of heat required to begin the operation.

When hydrated Fe_2O_3 is heated and placed over alcohol, its colour is deepened towards black, but not uniformly, and when cold the original colour returns. But if it be made red-hot and quenched in boiling alcohol out of contact with air, it is converted into hydrated Fe_3O_4 , and remains permanently a deep black magnetic powder, soluble in acids. A strong solution of ammonia may be substituted for the alcohol with the same effect, but in this case some of the sesquioxide will remain unaltered and mixed with the black oxide. The alcohol or ammonia is correspondingly changed by oxidation derived from the oxygen which has been released from combination with the iron. If the hydrated Fe_3O_4 be heated in contact with air, it immediately (even when it has been kept for many months) becomes Fe_2O_3 by oxidation from the atmosphere, but if heated to redness *in vacuo*, it cools unchanged. [Can the black powder of alumina be Al_3O_4 , formed in a similar way?] The process of catalysation by Fe_2O_3 is thus evident; the heated sesquioxide loses a portion of oxygen to the alcohol and becomes Fe_3O_4 , which is instantly reconverted into Fe_2O_3 by receiving oxygen from the air, and this alternation is constantly going on in every portion of the glowing mass. It is not a mere *action de présence*, but alternate reduction and oxidation of the sesquioxide, producing a continuous oxidation of the alcohol.

This suggests a consideration apparently adverse to the atomic hypothesis of Dr. Dalton. How can a single compound molecule Fe_2O_3 be changed by deoxidation into another compound molecule Fe_3O_4 , when, according to theory, there are in it but *two* combining proportions of iron, whereas the resultant contains *three*? and how (by deoxidation) can the resultant molecule contain *four* combining proportions of oxygen when the primary contained only *three*? We can indeed represent to the imagination that *three* molecules of the sesquioxide, acting as if they were one triple molecule, lose *one* combining proportion of oxygen, and are converted into *two* molecules of the black oxide; and conversely, that *two* molecules of the black oxide, acting as if they were *one* double molecule, combine with *one*

atom of oxygen, and are converted into *three* atoms of sesquioxide. The only way to account for this, in accordance with the popular atomic theory, seems to be, to assume that the notation for these oxides is incorrect, and that

for Fe_2O_3 we should write Fe_6O_9 ,
and for Fe_3O_4 we should write Fe_6O_8 .

If the current notation be retained, and any law be admitted, in virtue of which three molecules of sesquioxide may suffer reduction as if they were only one molecule, and divide into two molecules of the magnetic oxide, we might conceive a peculiar structure in the Fe_3O_4 , with a tendency to separate again into FeO , Fe_2O_3 ; that it is really in combination as Fe_3O_4 , but ready to yield to slight causes and become FeO , Fe_2O_3 . This would explain Mr. Mercer's experiment (quoted by Brande, I. 716, edition 1848) of the chemical union of a mechanical mixture of protoxide and peroxide of iron.

Perhaps the sesquioxides occupy a middle place in the scale of effects. Take the case of iron; we have

$\text{Fe} + \text{O}$, pyrophorus,—violent oxidation,
 $\text{Fe}_2\text{O}_3 + \text{NH}_3 + \text{O}$, alternate reduction and oxidation,
 $\text{FeO}_3 + \text{NH}_3$ (in water), reduction.

To show the last, add ammonia to a solution of FeO_3 , KO , and Fe_2O_3 will be precipitated.

A mixture of ten parts by weight of powdered chlorate of potassa with one part of Fe_2O_3 disengages oxygen with extreme facility and great economy of heat as compared with the oxides of copper and manganese; and it is the more convenient because n grains of the mixture will represent almost exactly n cubic inches of disengaged oxygen.

A state of mechanical division is not absolutely necessary for the catalysation of some inflammable vapours by Fe_2O_3 ; an old nail, entirely transmuted into rust, will perform the operation; and when we consider that in many cases of fermentation, decay and putrefaction, this oxide may be present, divided or aggregated, while heat is evolved, and inflammable gases and vapours are set free, we may hereafter be able to trace some instances of "spontaneous combustion" to the catalytic action of the sesquioxides of iron.

April 26, 1855. (Sir Benjamin Brodie, Bart., V.P., in the Chair.)

Note "On the position of Aluminum in the Voltaic series." By Charles Wheatstone, Esq., F.R.S.

Having, through the kindness of Dr. Hofmann, been permitted to examine a specimen of aluminum prepared by M. Claire-Deville, I availed myself of the opportunity to ascertain one of the physical properties of this extraordinary metal, which it does not appear has been yet determined, viz. its order in the voltaic series. The following are the results of my experiments.

Solution of potass acts more energetically and with a greater evo-

lution of hydrogen gas upon aluminum than it does on zinc, cadmium or tin. In this liquid aluminum is negative to zinc, and positive to cadmium, tin, lead, iron, copper and platina. Employed as the positive metal, the most steady and energetic current is obtained when it is opposed to copper as the negative metal; all the other metals negative to it which were tried became rapidly polarized, whether above or below copper in the series.

In a solution of hydrochloric acid aluminum is negative to zinc and cadmium, and positive to all the other metals above named. With this liquid also copper opposed to it as the negative metal gave the strongest and most constant current.

Nitric and sulphuric acids are known not to act chemically in any sensible manner on aluminum. With the former acid diluted as the exciting liquid aluminum is negative to zinc, cadmium, tin, lead and iron. The current with zinc is strong; with the other metals very weak, and it is probable that their apparent negative condition is the result of polarization. When aluminum is immersed in dilute sulphuric acid, this metal appears negative to zinc, cadmium, tin and iron, but with lead, on which sulphuric acid has no action, the current is insensible. In both these liquids copper and platina are negative to aluminum, and notwithstanding the apparent absence of chemical action on the latter metal, weak currents are produced.

It is rather remarkable, that a metal, the atomic number of which is so small, and the specific gravity of which is so low, should occupy such a position in the electromotive scale as to be more negative than zinc in the series.

PATENT.

Patent granted to Louis Faure, for Improvements in the Process for manufacturing Iodine.

THIS invention consists in the application and mode of applying sulphurous acid and chlorine to extracting iodine from the mother-liquors of nitrate of soda, and also from native nitrate of soda.

The following is the mode of treating native nitrate of soda and the mother-liquors therefrom, for extracting iodine therein contained in the state of iodic acid combined with soda, lime, or any other base:—Take about one quart of the mother-liquor of nitrate of soda of the strength of 36° to 37° Beaumé, and pour thereon, in small quantities, sulphurous acid held in solution in water from a graduated test-glass, continually agitating it until the precipitate of iodine freely separates from the liquid. When the liquid, which is slightly shaded, is filtered, it instantly loses its colour, and gives no sign of a further precipitate of iodine on the addition of 1 drop of sulphurous acid. This test should be repeated upon about 10 quarts.

and if the two results obtained correspond, 500 to 1000 quarts of mother-liquor can confidently be treated; for which it is merely necessary to employ a suitable proportion of sulphurous acid, and a vessel capable of containing a little more than 3 cubic feet of liquid.

The vessel to be employed should be of a circular form, and made of non-porous bricks, well luted, and afterwards lined with hydraulic cement. The diameter of the upper part of the vessel should be considerably less than that of the lower part, and should be hermetically closed by means of a wooden lid, well adjusted and lined internally with sheets of glass. The liquor is to be agitated in this vessel by means of a vertical shaft or agitator, provided with paddles, and set in motion by a winch and bevil-wheels. The paddles are inclined, and made of sandstone, and disposed for agitating violently the mother-liquors when the addition of sulphurous acid is made.

When the globules of gas which maintain part of the iodine precipitate on the surface of the liquor have been dispelled, the liquor is allowed to rest, and the supernatant liquor is then withdrawn by means of a sandstone siphon. The liquor is afterwards concentrated to extract the nitrate and sulphate of soda and chlorides of sodium and potassium.

The iodine precipitate is transferred to a sandstone fountain, at the bottom of which a filter is formed, composed of successive layers of quartz-stone finely powdered, and the grain of which decreases in size from bottom to top. After the iodine has been sufficiently drained, it is drawn off without disturbing the lower layer of iodine, and conveyed to a rectangular box, made of plaster of Paris, closed by means of a lid of the same composition, sliding friction-wise in two parallel grooves. The lid of the box should be thick enough (but not too compact) to allow the water of imbibition to filter into the sides and lid of the box. When the iodine is sufficiently dried, it is crystallized by sublimation.

To extract iodine from the mother-liquor in the state of iodate and iodide, the liquors are treated successively with a solution of chlorine and sulphurous acid, previously tested in the following manner:—When the liquor contains little iodide and much iodate, the iodine contained in the iodide is first precipitated by means of chlorine; and as soon as the reaction is terminated, a sufficient quantity of solution of sulphurous acid for decomposing the iodates is added. If the mother-liquor contains much iodide and little iodate, a solution of sulphurous acid is first employed, and afterwards an aqueous solution of previously tested chlorine. Several cubic feet of the mother-liquors may be treated at a time with precision and facility.

The above processes are economical and expeditious, and have the advantage of avoiding the loss of nitrate of potash or soda during the concentration of the liquors, which result cannot be effected by the employment of sulphuric acid of commerce by the ordinary method.—Dated Feb. 14, 1854.

THE CHEMICAL GAZETTE.

No. CCCIII.—June 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of the Phosphate of Lime existing in Animal Charcoal, Bone-ash, &c., with Remarks. By J. DENHAM SMITH.*

THE conviction of the value of phosphate of lime as a fertilizer has surely, and even rapidly, forced itself upon the farmer, and has thus created a new chemical manufacture in the kingdom, the products of which, under such names as "superphosphate," "phosphate manure," "dissolved coprolite," &c., are now extensively consumed in this country.

To furnish the phosphate of lime requisite to produce these manures, every source adequate to supply this salt in quantities sufficient for commercial purposes has been carefully sought out; and the phosphatic rocks of Estremadura and of the Northern States of America, the arenaceous deposits on various coral reefs in the Pacific Oceans, the residues of the vast slaughter-houses of the La Plata, the refuse animal charcoal of the European sugar-refiners, and the coprolitic beds of this island, have hitherto abundantly furnished the manufacturer with the raw material of these composts.

These raw materials, especially the three last,—bone-ash, refuse animal charcoal and coprolite,—have under these influences become articles of trade of sufficient importance to render an exact method of determining their value, by ascertaining the amount of phosphate of lime they contain, necessary to the dealer, the manufacturer and the farmer. To effect this determination, the mode adopted by the analyst has, I believe, usually been that directed by Gmelin† for preparing "ordinary phosphate of lime," "triphosphate," "bone-earth," &c., by dissolving bone-ash in hydrochloric or nitric acid, expelling the carbonic acid by boiling, precipitating by ammonia, washing, igniting, and weighing the precipitate.

This mode of analysis had been the one employed for commercial purposes by my friend Mr. E. F. Tschernacher and myself, to determine the per-centage of phosphate of lime a sample of animal charcoal, &c. submitted to us for examination might contain, without suspicion of inaccuracy attaching to it until during the last year; when, owing to several instances wherein the analyses of some

* Communicated by the Author.

† Works of the Cavendish Society, L. Gmelin, vol. iii. p. 192.

of our contemporaries and our results differing greatly the one from the other, forced the subject of the constitution of the phosphate of lime existing in animal charcoal, bone-ash, and other natural products, on our consideration.

On repeating our analyses of various samples, we found that the above method of determining the amount of the phosphatic earth could not be relied upon as furnishing uniform, let alone accurate results; and that in several determinations varying, hap-hazard, in the nature of the acid solvent, the state of dilution of the solution, the temperature at which precipitation was effected, the strength of the precipitant, and the general conditions under which the analysis was conducted, yielded with the same sample, sometimes similar, sometimes widely differing results. I quote a few instances:—

Per-centage of precipitated phosphate of lime from four specimens of animal charcoal:—

Sample	I.	II.	III.	IV.	V.
A	$73\frac{1}{4}$	$66\frac{1}{2}$			
B	$69\frac{1}{2}$	$63\frac{3}{4}$	$64\frac{1}{4}$	$69\frac{1}{2}$	$66\frac{3}{4}$
C	$68\frac{1}{2}$	71	$63\frac{1}{4}$	$66\frac{1}{2}$	
D	72	$73\frac{1}{4}$			

Such results were conclusive. Not merely did we differ with others, but we differed with ourselves; and nothing remained but to cast this method aside as worthless.

The question next to be solved was that of the composition of these various phosphates, whether they presented a uniform or a diverse composition.

Referring again to Gmelin's 'Handbook' (*vid. supra*), we find three analyses quoted, all differing from each other, and all leading the authorities cited to different conclusions respecting the constitution of ordinary phosphate of lime. Reducing the analytic results, on the *data* of the equivalent of phosphoric acid being 72 and that of lime 28, the ratio of acid and base will be as under:—

	Berzelius.	Fuchs.	Thilenius.
Phosphoric acid	72	72	72
Lime	77	86	97

numbers from which no atomic constitution can be rigidly deduced, although that of Fuchs approximates too closely to the formula of the tribasic phosphate ($\text{PO}_3 \cdot 3\text{CaO}$) to leave any doubt of the excess of lime in this instance being due merely to manipulatory error. Frémy, in his elaborate paper on Bones, recently published in the 'Annales de Chimie,' states the phosphatic earth of bones to be a tribasic phosphate; but this statement applies to the phosphate present in recent bones, and not to that in those which have been burnt.

Finding how widely our predecessors in this inquiry differed with each other, Mr. Teschemacher and I submitted six specimens of precipitated phosphate of lime to analysis. The three first, E, F, G, are from different samples of animal charcoal; the three last are

from one sample of bone-ash; H being thrown down from a dilute boiling solution in muriatic acid by ammonia, K precipitated in like manner from a solution in nitric acid, and L from a nitric acid solution, well boiled, cooled, very much diluted, precipitated with diluted solution of ammonia, and washed with cold water; this last, after ignition, yielded the well-known, hard, horny, semi-porcellaneous phosphate of lime; whilst H and K were opaque, soft, and chalky to the touch:—

		Phosphoric acid.	Lime.
Phosphate of lime	E	72	90
„	F	72	86.50
„	G	72	80
„	H	72	82
„	K	72	80.80
„	L	72	83.70

The above numbers have been calculated from the several analytic results on the data before used of $\text{PO}^5=72$ and $\text{CaO}=28$; and but confirm the general results pointed at by the analyses of Berzelius, Fuchs and Thilenius, viz. that precipitated phosphate of lime varies in composition, and leads to the belief that temperature, state of dilution, washing, &c., somewhat modify its constitution, so that it consists, after ignition, of a tribasic phosphate, mixed with varying proportions of a more or less basic phosphate; and shows the truth of the opinion of Berzelius, that the composition of the phosphate of lime in bones must be a subject of uncertainty. It is well to add here, that the estimation of the composition of these several phosphates was effected by means of oxalic acid, deducting the magnesian phosphate contained in the lime-salt from the weight operated on. The very close approximation of L (83.70 of lime instead of 84) to the tribasic salt deserves notice.

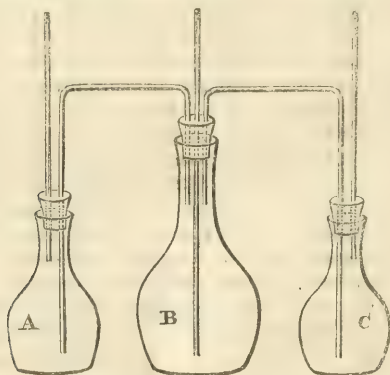
Both Mr. Teschemacher and myself had, formerly, constant occasion to remark, that the sum of the results of an analysis of animal charcoal, &c. usually exceeded the weight operated upon, assuming the sample to consist of phosphate of lime and magnesia, as precipitated, carbonate of lime, sulphate or sulphuret of lime (if any of either), moisture, carbon, sand, alkaline salts, &c.; and although lime sometimes exists free and uncombined in bone-ash to a noticeable amount, yet in animal charcoal and coprolites this never occurs, at any rate we have never met with it; and as both carbonate and sulphate of lime possess a definite and never varying composition, it is evident, that whatever lime exists in a sample of animal charcoal or bone-ash (exempt from this earth in a free state), over and above the quantity required to saturate the carbonic and sulphuric acids, must be combined with the phosphoric acid, and that this may be more or less basic than the tribasic, or the $3\text{PO}^5, 8\text{CaO}$ phosphate of lime, according to a vast number of conditions unnecessary here for me to enter upon; all we can arrive at with certainty being, that the quantity of phosphate of lime occurring in a given sample of animal charcoal is the phosphoric acid *plus* the lime uncombined with other acids.

Careful investigation of the causes of the analytic excess before referred to, proved that the phosphate of lime occurring in the commercial product was, as a rule, more basic, and often considerably more basic, than the precipitated phosphate of lime that raw material yielded on analysis; and that from the filtrate more carbonate of lime was obtained than was indicated by the carbonic acid and sulphuric acid (if any) afforded by the sample. Moreover, when the carbonic acid indicated by experiment (the amount of which was estimated by a modification of Will's apparatus hereafter described) was taken as the *datum* on which the amount of carbonate of lime was to be estimated, and the carbonic acid deducted from the excess of the carbonate of lime produced in analysis, retaining the resulting lime alone in estimating the constituents of a sample of bone-ash, the sum of the analytic results then so closely approximated to the weight originally taken, as to convince us that any slight loss or gain was mere error of manipulation.

I might here close these observations so far as the principles involved are concerned; but as the description of the mode of analysis now adopted by Mr. Teschemacher and myself, for determining the quantity of phosphate of lime existing in animal charcoal, &c. may be of interest to some of the readers of the 'Chemical Gazette,' I subjoin the plan we pursue.

It is obvious that two methods are open to our choice, viz. the indirect, that of determining all the constituents of the sample excepting the lime-phosphate, and deducing its amount from the deficiency; or the direct method, a plan always to be followed as a rule by the analyst, unless forced by circumstances to adopt the inferential mode of estimation. We therefore employ the direct method.

To estimate the Carbonate of Lime.—To the various modifications of Will's apparatus I have now to add another, which is new to me, although likely enough to have been planned by any one else. It



is fitted of course for the determination of the carbonic acid of all carbonates whose bases form insoluble, or but slightly soluble salts with sulphuric acid; it is also facile in use, which is more than can

be said of most of these modified apparatus. To the usual pair of small light flasks I add a third and central one, of somewhat greater capacity than the other two. To the flask A, intended for dilute nitric acid, a cork is fitted, into which a straight tube passes, reaching to a convenient height above the cork; and besides this, a second tube, bent at two right angles; the leg which is inserted in flask A reaches nearly to the bottom of the flask, so that on pressure the liquid shall flow into flask B, through the cork of which the short feeding leg of this tube passes. Flask B, the central one for the reception of the animal charcoal, has a straight safety-tube, and another double right-angled tube (which latter connects it with flask C) passing through its cork; whilst flask C, containing sulphuric acid, has, besides the longer leg of the foregoing right-angled tube, a piece of straight tubing, just as is seen in the acid flask of Will's apparatus, passing through its cork. The three straight tubes are fitted with corks, to stop their apertures as occasion may require. This apparatus being thus constructed, it is evident that if diluted nitric or hydrochloric acid be placed in A, the ground animal charcoal in B, and sulphuric acid in C, on stopping the straight tube of B, slightly loosening the cork in A's straight tube, and sucking at C, that the dilute acid in A will flow into B through the right-angled tube, and on corking A's tube the carbonic acid liberated will pass through the sulphuric acid in C; and from the loss of weight the amount can be determined with exactness. In practice I find nitric acid, P.L., previously boiled and diluted with about four times its bulk of water, is a good strength for use; and that not less than 200 grs. of material should be operated upon, and this moistened with a little water. As but little heat is generated, it is *essential* to heat flask B and its contents, so as to expel all the carbonic acid. The apparatus, when charged, is necessarily somewhat heavy; but with an Ærtling's balance, capable of bearing a pound at each end, and indicating one-tenth of a grain, it affords most exact results when tested with Iceland spar. The loss of weight, when the apparatus is cold, indicates the amount of carbonic acid, and consequently that of the carbonate of lime contained in the sample under examination.

The sulphuric acid and sulphur, if any and if existing in combination with lime, are to be determined by baryta in the usual manner.

It is convenient, to save time, to employ a separate quantity, say 50 or 100 grs., of the substance under examination, to determine the lime-phosphate. Thus when 100 grs., in fine powder, are treated with diluted nitric acid, strength as above, and the mixture warmed, all the lime-salts will be dissolved; this filtered, the residue well washed, the filtrate boiled to expel any carbonic acid, and then largely diluted and precipitated by excess of solution of ammonia, yields a phosphate of lime, which, if these operations and the subsequent washings be conducted at nearly a boiling heat, separates most readily on the filter, and is quickly and easily washed; this precipitate is to be dried, ignited and weighed. To the ammoniacal

filtrate, solution of sesquicarbonate of ammonia is added, which throws down the remainder of the lime as carbonate; this is to be collected, washed, and weighed in the usual manner.

We have now all the *data* required for estimating the results of the analysis for commercial purposes. From the weight of carbonate of lime obtained, say 15 grs., deduct that indicated as existing in the animal charcoal by the carbonic acid apparatus, say 10 grs., leaving 5 grs. in excess; reduce this to lime = 2.80 grs.; saturate any sulphuric acid, say 0.40, with lime = 0.28, which leaves 2.52 grs. of lime to be added to the weight of the precipitated phosphate, the sum of which will indicate the actual quantity of phosphate of lime and phosphate of magnesia existing in a given sample, the composition of which phosphate evidently varies greatly in the several samples, it usually being somewhat more basic than $\text{PO}_5 + 3\text{CaO}$. The amount of carbon, sand, &c., alkaline salts and moisture, may be estimated in the usual way, should the analyst so desire. With bone-ash, containing free lime, carbonate of ammonia affords a ready means of estimating the amount of the uncombined lime; otherwise the *modus operandi* is exactly similar to that above detailed. With coprolite greater difficulties accrue, containing, as it frequently does, phosphate, carbonate and sulphate of lime, phosphate of magnesia, phosphate, sulphuret and hydrated peroxide of iron, alkaline salts, clay, sand, moisture, organic matter, &c.; an exact analysis is next to impossible, and the dealers in the article could neither afford the time nor money such an examination would require; so that it may for their purposes be advisable to convert the basic iron phosphate into phosphate of soda by means of the carbonate of that alkali, and estimate the phosphoric acid as if it were in combination with lime alone.

On Metallic Tungsten and Molybdenum. By F. WÖHLER.

Metallic tungsten may be obtained, as I found some time ago, in the form of a compact brilliant mirror, when chloride of tungsten and dry hydrogen are together passed through a red-hot glass tube. Experiments, which have been made at my instance by Dr. v. Uslar, have shown that it is immaterial whether the pale yellow oxychloride or the dark red chloride be used. This is a proof that the body so obtained is really the metal itself, and not a lower degree of oxidation of it.

The metal separated from these two chlorides showed also, on being oxidized to tungstic acid, an increase of weight, which almost exactly agreed with the theory.

The metallic tungsten thus obtained shows on the glass side a very brilliant, dark, steel-coloured, metallic mirror. On the other side, it shows a lighter, dull iron colour. Part of it remains adhering to the glass, but a part of it may also be separated in the form of tubes, an inch long, as thick as paper. It is quite brittle and very hard. According to the determinations of Dr. von Uslar, its specific gravity is 16.54. The specific gravity of a preparation of the metal in pow-

der, which I reduced from nitride of tungsten, was found by Dr. von Usler to be 17.5; while a specimen, also in the form of powder, but reduced by hydrogen from crystallized acid tungstate of potash, gave 18.26 spec. grav. The temperature was for all these determinations 70° F. According to earlier statements, the specific gravity of the fused metal varied from 17.2 to 17.6.

On being heated in the air, it becomes on the surface of a steel-blue colour, inflames, and burns to yellow tungstic acid. In the interior there always remains a small quantity of unoxidized metal; so that it was only by igniting the very finely powdered metal in oxygen, that Dr. von Usler obtained the correct increase of weight.

Tungsten in this state is changed by no acid, not even aqua regia; concentrated potash ley is also without action upon it. On the other hand, it is easily dissolved by a mixture of potash ley and solution of hypochlorite of soda.

Dr. von Usler tried to obtain metallic tungsten by melting its tersulphide with excess of cyanide of potassium. Sulphocyanide of potassium was obtained, and a black substance, which proved to be bisulphide of tungsten, and which was not altered by a new fusion with cyanide of potassium.

Molybdenum may also be obtained, like tungsten, from its chlorides by heating them in dry hydrogen. Dr. von Usler obtained it in the form of a strongly-shining, clear, steel-coloured, metallic mirror, which was on the inside of a lighter, dull, tin-white colour. It was easily separated from the glass, and showed a certain malleability. It was obtained in the form of metallic foil of a silver colour, and apparently melted by heating molybdic acid in a small porcelain tray in a porcelain tube to a strong red heat, and passing dry hydrogen over it.—Liebig's *Annalen*, vol. xciv. p. 256.

On the Decomposition of the Fluorides by means of the Pile.

By M. E. FREMY.

The interesting facts lately ascertained by M. Bunsen, which are remarkably related to those formerly studied by M. Becquerel, have called the attention of chemists to the advantage which might be derived from the employment of electrolytic decompositions in obtaining new bodies. Wishing to retain a priority in a question which I consider as of great importance, and with which I have long been occupied, I will lay before the Academy the results which I have obtained by submitting the fluorides to the action of the pile. The object of my experiments has been, not to disengage the metals from their binary combinations, but to isolate fluorine; they differ in this respect from those of M. Bunsen.

The decomposition of the fluorides could only be attempted with very pure fusible compounds. My first attempts, which were made three years ago, were with absolutely pure fluoride of calcium. By melting this body, and submitting it to the action of an electric current, I found that a brisk effervescence was produced in the mass, and that a gas which acted upon glass was evolved from the positive

pole; at the negative pole calcium was deposited, which the oxygen of the air immediately converted into lime.

This experiment, important in a theoretical point of view, did not enable me to study the properties of fluorine; fluoride of calcium is only fusible by a forge-heat, and at this temperature it is not easy to pursue one's observations; the platinum crucible also is soon eaten through by the fused fluoride of calcium.

I then submitted to the influence of the pile other more fusible fluorides, such as those of tin, lead and silver; but in this series of experiments I met with new difficulties, which still prevented me from arriving at the result for which I sought.

The metallic fluorides just mentioned are indeed decomposed with facility by the pile; but the metal eliminated combining with the platinum of the vessel in which the fluorides are kept fused, perforates it in a few moments. Moreover, the preparation of neutral and absolutely pure metallic fluorides is always difficult; these salts are usually acid, or hydrated, or mixed with oxyfluorides produced by the action of water upon the neutral fluorides; when these are submitted to the action of the pile, they furnish a gaseous mixture composed of fluorine, oxygen and hydrofluoric acid.

After these fruitless efforts, I was led to operate upon the fluorides of potassium and sodium, which are certainly less fusible than the fluorides of lead and tin, but which may be obtained in a state of absolute purity. Thus fluoride of potassium, upon which nearly all my experiments have been made, and which I have always prepared by calcining hydrofluat of fluoride of potassium in a vessel of platinum protected from the air, actually contains nothing but potassium and fluorine.

The decomposition of this salt was effected in the following apparatus. A tubulated platinum retort contained the alkaline fluoride, which I kept in a state of fusion by means of a good forge. A platinum wire, communicating with the positive pole of the pile, was immersed in the fused fluoride, while the walls of the retort were connected with the negative pole. As soon as the fluoride is submitted to the influence of the electric current, it is rapidly decomposed; the platinum wire which dips into the fluoride is attacked by the fluorine, and converted instantaneously into fluoride of platinum, which is itself quickly decomposed by the action of the heat, forming platinum sponge, which is found in the retort after the experiment. I have hitherto found it impossible to replace the platinum wire by a stick of charcoal, as this, when pure, is rapidly disintegrated in the fluoride, and when it is coherent contains silica or other mineral substances, which the fluorine immediately attacks. Through the neck of the platinum retort an odoriferous gas passes off, which decomposes water, forming hydrofluoric acid, and displaces the iodine contained in iodides. This gas appeared to me to be fluorine. But the wasting of the platinum conductor, and the solidification of the mass which is constantly being projected upon the walls of the retort, unfortunately soon put an end to this interesting experiment.

Taking into consideration the properties of the gas produced in the preceding experiment, and that this body attacks platinum in the same way as chlorine, phosphorus or sulphur, I think myself able to announce to the Academy, that I have actually isolated, by means of the pile, the radical contained in the fluorides, and that this body appears to me to be identical with that which I had previously obtained by decomposing certain fluorides by oxygen at a very high temperature.

These researches, which present difficulties of every kind, are far from being terminated. I am at this moment arranging some platinum vessels, in which I hope to avoid the solidification of the fluoride, and especially the action of the air, which, by oxidizing the alkaline metal, produces a binary compound, which is decomposed by the pile at the same time as the fluoride.—*Comptes Rendus*, April 23, 1855, p. 966.

On some supposed Aldehydes and Acetones. By Dr. LIMPRICHT.

Limpricht has found that the following bodies, considered to be aldehydes and acetones, give no compounds with bisulphites of the alkalies; and concludes hence that they are either not aldehydes or acetones, or that the property of combining with bisulphites of the alkalies is not common to all aldehydes or acetones:—

Myristone, prepared from the dry distillation of myristate of lime; a mixture of *palmitone* and *stearone*, obtained by heating rapidly margaric acid with excess of lime; and

Benzophenone, prepared in the same way from benzoate of lime; *phorone*, from camphorate of lime; *palmitinaldehyde*, by the oxidation of spermaceti with chromate of potash and sulphuric acid.—*Liebig's Annalen*, vol. xciv. p. 243.

On Hypogæic Acid. By MM. GÖSSMANN and SCHEREN.

Gössmann and Scheren, in an investigation of earthnut-oil, have found, that besides the arachnic acid already found in it by Gössmann, it contains a fatty acid of the so-called oleic acid series of the general formula $C^n H^{n-2} O^4$. This acid they have named hypogæic acid, and it has the formula $C^{32} H^{30} O^4 = C^{32} H^{29} O^3 + HO$.

Its preparation was as follows. The earthnut-oil was saponified in the usual way, the fatty acids separated, and purified by repeated meltings in water. The acids were then dissolved in a sufficient quantity of alcohol, and acetate of magnesia and ammonia added to precipitate the arachnic acid, &c. The filtrate was then mixed with acetate of lead and excess of ammonia, and allowed to stand some days. When the precipitate no longer increased, it was collected, dried by pressing as quickly as possible, and treated with æther in a well-stoppered vessel.

The ætherial solution of the lead-salt was decomposed with a slight excess of hydrochloric acid, access of air being prevented as much as possible, the chloride of lead filtered off, and the filtrate frequently agitated with water. After the ætherial solution of the oleic acid had separated out quite clear, it was removed, and pre-

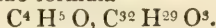
served in a well-stoppered vessel till the cold weather permitted its further investigation. When this commenced, the greater part of the æther was evaporated in the water-bath. On cooling, a somewhat yellowish acid crystallized out, which was collected, gently pressed, and on being recrystallized out of alcohol, was obtained quite white and in needle-formed masses. A yellowish acid remained in the mother-liquor, which had probably been changed by oxidizing influences. At a low temperature this also crystallized out, and by recrystallization from alcohol at a low temperature could be readily obtained colourless.

These various purified crystallizations formed the new acid, which has the following properties :—It consists of colourless needle-formed masses, melts at 93° to 95° F., is easily soluble in alcohol and æther, is easily saponifiable at the ordinary temperature, by action of the air becomes yellowish or reddish, has then an extremely rancid smell, and reacts acid. The altered acid crystallizes very difficultly only by an intense cold. These properties it has, to a certain degree, in common with the ordinary oleic acid.

The analyses of the purified oil gave results almost exactly corresponding with the theory.

The formulæ of the neutral salts is $\text{MO}, \text{C}^{32} \text{H}^{29} \text{O}^3$. Analyses of the copper and lead salts gave also very exact results.

The æther was prepared by passing hydrochloric acid gas into a solution of the acid in alcohol. It is formed very easily, and as it is pretty insoluble in alcohol, it was easily separated from an admixture of acid, and thus obtained pure. It is yellowish coloured, without smell, heavier than alcohol and lighter than water. It was dried in a stream of carbonic acid at a temperature of 212° to 248° F. Analyses of the body thus prepared gave numbers which agreed very well with the formula—



Gössmann and Scheren made experiments to see if another oleic acid were contained in the oil, but found that this was not the case.

They are still occupied with the subject.—*Ann. der Chem. und Pharm.*, vol. xciv. p. 230.

On the Preparation of Leucine. By Dr. LIMPRICHT.

The ammonia compound of valeraldehyde (obtained by distilling fusel-oil with bichromate of potash and sulphuric acid) is boiled in a retort with hydrocyanic and hydrochloric acids, till the layer of oil, which consists of the melted ammonia compound, has disappeared. The greater part of the sal-ammoniac is then separated by crystallization; the hydrochloric acid is removed by hydrated oxide of lead, and the excess of lead by sulphuretted hydrogen. The filtrate from the sulphuret of lead is evaporated to dryness on the water-bath, and the residue crystallized from weak spirit. The crystals show all the reactions and the composition of leucine*.—Liebig's *Annalen*, vol. xciv. p. 243.

* The probability that leucine could be formed in the above manner has been already expressed by Gössmann in a paper on leucine, which appeared in the '*Annalen der Chemie und Pharmacie*,' June 1854.—*Translator*.

Analysis of Indian Corn, Wheat, &c.
By ARCHIBALD POLSON, Paisley*.

I have lately been engaged with the analysis of several well-known farinaceous substances, with the view of ascertaining their relative values as starch-yielding materials.

As the results, which were determined with the greatest care, may prove useful to manufacturers and others interested in similar inquiries, I have arranged them in the two following tables, showing their composition in the dried and undried states:—

TABLE I.—*In the commercial or undried state.*

	Indian corn.				Wheat.		Beans.		Barley.	Beer.	Rice.	Millet.
	Flat white American.	Flat yellow American.	Round yellow American.	Round yellow Galatz.	Old American.	New Scotch (6 months old).	Old Irish.	Egyptian.	New Scotch (6 months old).	New Scotch (6 months old).	Patna (cleaned).	Egyptian.
Water	11.8	11.5	13.2	11.8	10.8	14.8	12.8	10.8	12.0	12.6	9.8	8.0
Ash	1.8	1.6	1.6	1.8	1.6	1.5	1.8	1.8	2.8	2.2	0.9	1.8
Gluten	8.9	8.7	8.9	9.1	10.9	7.0	24.7	26.6	13.2	13.0	7.2	10.1
Starch	51.8	53.5	54.8	50.1	62.3	56.9	36.4	31.5	52.7	49.7	78.8	49.0
Husk and veg. fibre	15.9	16.5	14.9	20.4	8.3	12.4	17.6	18.8	11.5	14.3	0.2	25.4
Fat	4.4	4.7	4.4	4.5	1.2	1.2	2.4	2.8	2.6	2.6	0.1	3.1
Gum and sugar ...	2.9	2.3	2.9	2.9	3.8	5.3	4.6	6.5	4.2	4.5	1.6	1.5
	100.5	98.8	100.7	100.6	98.9	99.1	100.3	98.8	99.0	98.9	98.6	98.9

TABLE II.—*In the dried state (dried at 212°).*

	Indian corn.				Wheat.		Beans.		Barley.	Beer.	Rice.	Millet.
	Flat white American.	Flat yellow American.	Round yellow American.	Round yellow Galatz.	Old American.	New Scotch (6 months old).	Old Irish.	Egyptian.	New Scotch (6 months old).	New Scotch (6 months old).	Patna (cleaned).	Egyptian.
Ash	2.0	1.8	1.8	2.0	1.9	1.7	2.0	2.0	3.1	2.3	1.0	2.0
Gluten	10.1	9.9	10.2	10.3	12.2	8.3	28.4	30.0	15.1	14.9	8.0	10.9
Starch	62.2	60.4	63.5	56.8	69.9	66.9	41.9	35.4	60.1	57.4	87.2	53.5
Husk and veg. fibre	18.0	18.6	16.6	23.1	9.3	14.6	20.0	21.0	13.0	16.2	0.2	27.6
Fat	4.9	5.3	5.1	5.1	1.3	1.4	2.7	3.1	3.0	3.0	0.1	3.3
Gum and sugar ...	3.3	2.8	3.5	3.3	4.3	6.2	5.3	7.3	4.7	5.1	2.1	1.6
	100.5	98.8	100.7	100.6	98.9	99.1	100.3	98.8	99.0	98.9	98.6	98.9

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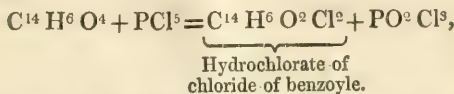
* Communicated by the Author.

On the Action of Protochloride of Phosphorus upon a Series of Monohydrated Acids. By M. BÉCHAMP.

M. Cahours has obtained several chlorides of organic radicals by the action of perchloride of phosphorus upon the corresponding monohydrated acids*. The reaction for the chloride of benzoyle is expressed by the equation,—



M. Gerhardt has pointed out with reason that the action of the perchloride of phosphorus upon the organic acids is not only a double decomposition, but that it consists of two successive actions, as proved by the evolution of hydrochloric acid; and this chemist formulizes the decomposition of benzoic acid in the unitary system as follows :—



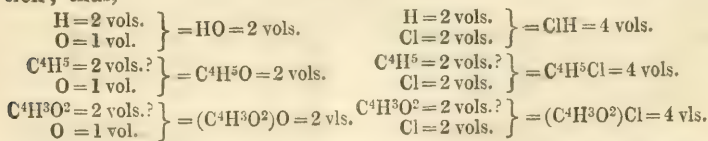
the hydrochlorate of chloride of benzoyle which appears to be formed being afterwards decomposed into hydrochloric acid and chloride of benzoile,—



We shall soon see that this result is capable of a more simple interpretation, but must observe in passing, that the chlorine in the hypothetical compound $\text{C}^{14} \text{H}^6 \text{O}^2 \text{Cl}^2$ would be fulfilling two different parts, as M. Regnault has proved to be actually the case in the chlorinated hydrochlorates of bicarbonated hydrogen.

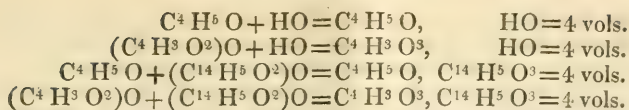
M. Gerhardt afterwards obtained several other organic chlorides by the action of oxychloride of phosphorus upon the potash salts of certain monobasic acids, such as the acetate and butyrate of potash. I have succeeded in preparing these compounds in a more simple manner, by the action of the protochloride of phosphorus upon monohydrated butyric and acetic acids. I was led to this result by the two following considerations :—

I. It is remarkable,—1st, that the simple æthers, the anhydrous acids of the monobasic acids, and the corresponding chlorides, have an equivalent represented by 2 or 4 vols. of vapour, and are comparable to water or hydrochloric acid as to their mode of condensation; thus,—



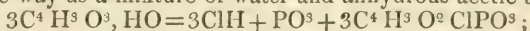
and, 2nd, that the æthers of the best-characterized monobasic acids contain, like alcohol, 4 vols. of vapour in their equivalent, and that the equivalent of these monohydrated monobasic acids is itself represented by 4 vols. of vapour, as well as the double anhydrides of M. Gerhardt; thus,—

* Chem. Gaz., vol. vi. p. 417.



II. The protochloride of phosphorus is decomposed when in contact with water, giving rise to hydrochloric acid; if anhydrous acetic acid be comparable to water, it should be decomposed when in contact with protochloride of phosphorus, with evolution of chloride of acetylene, whilst monohydrated acetic acid should furnish hydrochloric acid, chloride of acetylene and phosphorous acid. I tried this experiment, and it resulted as I had foreseen.

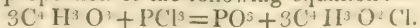
If monohydrated acetic acid* be treated with protochloride of phosphorus, the two liquids are seen to mix at first, the protochloride dissolving in the acid; but the evolution of hydrochloric acid gas commences immediately, even at the temperature of 59° F. I put the mixture into a sealed tube; the liquid soon became turbid, and a substance, the viscosity of which increased insensibly, was precipitated when the tube had been exposed for some time to a temperature of 86° to 104° F. The operation appearing to be completed, I broke the narrow point of the tube, when a torrent of hydrochloric acid was evolved. The very mobile part of the liquid contained in the tube was nearly pure chloride of acetylene, which distilled over almost entirely between 129° and 135° F. The residue of the distillation was hydrated phosphorous acid; in fact, this viscous residue dissolved in water without evolution of gas, and the solution reduced bichloride of mercury to the state of protochloride and nitrate of silver to metallic silver; lastly, if a part of this residue was heated before adding water to it, phosphuretted hydrogen was soon evolved, which inflamed in the air. Thus monohydrated acetic acid in contact with protochloride of phosphorus is decomposed in the same way as a mixture of water and anhydrous acetic acid,—



only that, by a secondary action, the nascent phosphorous acid dehydrates a part of the acetic acid, and anhydrous acetic acid is formed, which in its turn is converted into chloride of acetylene, as should be the case theoretically, and is proved by the following experiment:—

I converted the chloride of acetylene of the preceding operation into anhydrous acetic acid by distilling it with fused acetate of soda. The product, distilled upon a fresh portion of acetate of soda, was finally rectified so as only to collect what passed at 278°·6 F. I ascertained that this anhydrous acid did not contain any trace of chloride of acetylene.

Anhydrous acetic acid and protochloride of phosphorus were mixed in the proportion of the following equation:—

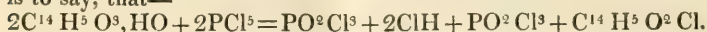


The protochloride dissolves in the anhydrous acid without any trace of evolution of gas. The mixture was put into a sealed tube, when no reaction takes place at the ordinary temperature even after

* The acid which I employed was crystallized at 61° F.

several hours; but if it be heated in the water-bath, the mixture becomes suddenly turbid when the temperature of the bath reaches about 149° F. A solid and very white substance separates; it becomes yellow towards 176° F. On breaking the tube, I observed no escape of gas. The liquid portion was distilled; it all passed between 131° and 140° F. It consisted of chloride of acetylene without a trace of chloride of phosphorus. The solid part was only anhydrous phosphorous acid impregnated with chloride of acetylene.

The decomposition of monohydrated acetic acid therefore takes place in two periods. The two liquids mix at first, but hydrochloric acid is soon disengaged, the mixture becomes turbid, hydrated phosphorous acid separates, and chloride of acetylene is produced. If this be really the case, the decomposition of the monohydrated acids by perchloride of phosphorus would also take place in two periods, that is to say, that—



I have commenced some experiments, from which it appears that all the monobasic acids undergo the same kind of decomposition as acetic acid with protochloride of phosphorus.—*Comptes Rendus*, April 23, 1855, p. 944.

On an easy Method of preparing the Oil of Olefant Gas.

By Dr. LIMPRICHT.

A tubulated retort, to which a receiver is attached, is half-filled with a chlorine mixture, consisting of 2 parts manganese, 3 parts chloride of sodium, 4 parts water, and 5 parts sulphuric acid. Through the tubulure of the retort a glass tube is fitted, which dips half an inch in the chlorine mixture, and which is connected with an apparatus for the production of olefant gas. Where coal-gas is at hand, it will be the most advantageous source; but in other cases it is easily prepared from alcohol and sulphuric acid. By mixing these with sand to a thick paste, all frothing is avoided. At the beginning of the operation an extremely gentle heat is applied, and it is only towards the last that it is necessary to raise the heat to distil over the product formed.

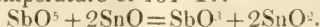
2 oz. of alcohol gave in an hour and a half a distillate, which on rectification afforded 1 oz. pure chloride of ethyle.—*Liebig's Annalen*, vol. xciv. p. 243.

ANALYTICAL CHEMISTRY.

On the Volumetric Determination of Antimony.

By Dr. A. STRENG.

As I had previously supposed, antimony may also be determined by means of protochloride of tin and bichromate of potash. Thus if the antimony be converted into antimonious acid (dissolved in muriatic acid and alcohol), and an excess of protochloride of tin be added to it, a complete reduction to the state of oxide of antimony takes place at a temperature of 104° F.:—



This reduction takes place even at the ordinary temperature, but more slowly than at 104° F. The strength of the solution of tin, as well as its excess, may be determined by a standard solution of bichromate of potash.

The following is the process. The substance containing antimony is dissolved in muriatic acid, with an addition of alcohol if necessary; chlorate of potash is added, and the whole is left in a moderately warm place until the odour of chlorine has entirely disappeared. If the temperature be raised too high, in order to hasten the volatilization of the chlorine, some of the chloride of antimony is volatilized at the same time. When the temperature of the fluid still remains a little above 104° F., a measured quantity of a normal solution of tin is added, and the whole, after being well stirred, is left standing for five minutes. After the addition of 3 drops of iodide of potassium and starch-paste, the excess of protochloride of tin is ascertained by means of the chromic solution.

At first I made use of a burette for measuring off the solution of tin, but I have since chosen a more simple instrument for this purpose. A globe-pipette is blown from a rather narrow, but thick-walled glass tube, so as to contain from 8 to 12 cub. centims., and this is marked with a file a little above the globe. This pipette, the exact contents of which it is not necessary to know, serves for measuring off the solution of tin; it is filled exactly to the mark, and emptied into the fluid to be reduced, with the precautions necessary in pipette operations. If this quantity of protochloride of tin be insufficient for complete reduction, the pipette must be filled, without washing, for a second or third time up to the mark. To determine the strength of the solution of tin, the pipette is again filled, and the amount of protochloride of tin contained in one pipette is ascertained by means of the solution of bichromate of potash.

The per-centage amount of oxide of antimony in any substance is obtained by the following formula:—

$$x = \frac{100 \cdot 3\text{SbO}_3}{2 \cdot A \cdot \text{KO} \cdot 2\text{CrO}_3} c(\text{CG} - \text{K}),$$

in which A indicates the amount of substance employed, c the value of 1 cub. centim. of the chrome solution, G the number of times the pipette has been filled with the solution of protochloride of tin, C the number of cubic centimetres of the chrome solution required for one pipette-charge of the tin solution, and K the quantity of the chrome solution representing the excess of the tin solution.

If the constant values in the formula be calculated, it acquires the following form:—

$$x = \frac{154 \cdot 47 \cdot c}{A} (\text{CG} - \text{K}).$$

If c be made to equal 0.01, and $A = 1.54447$, the equation

$$x = \text{CG} - \text{K}$$

gives the per-centage amount of oxide of antimony.

In order to test the process, the following experiments were instituted. Tartrate of potash and antimony was pulverized, dried for a

day at 212° F., and the amount of oxide of antimony contained in it ascertained:—

	I.	II.
A =	0.5 gr.	1 gr. tartar emetic.
G =	1	3 ...
C =	23.13	17.16 ...
K =	8.5	22.5 ...
c =	0.01	0.01 ...

Found.

	I.	II.	Calculated.
Per-centage amount of SbO^3 ..	45.2	44.72	46.06

For the calculation of metallic antimony or antimonious acid, the formula must of course be altered, and the proper atomic weights introduced.

This method may very readily be employed in an analysis by weight, when sulphuret of antimony has been precipitated by an acid from its solution in sulphuret of ammonium, and filtered. The precipitate is put with a filter into a beaker; it may then either be treated with muriatic acid and chlorate of potash, and digested at a gentle heat until all the antimony is dissolved and all the free chlorine has disappeared, or mixed with hydrate of potash and water, and dissolved by the passage of chlorine through it at 122° F. After the addition of a large quantity of alcohol and supersaturation with muriatic acid, it is gently heated until the odour of chlorine has disappeared, when the solution is treated with protochloride of tin and bichromate of potash.

In this manner I made a purely volumetric analysis of a lead slag, from the Lautenthal works. I digested the alloy for a long time with nitric acid, and after the complete oxidation of the lead and antimony, supersaturated it with ammonia and sulphuret of ammonium, and heated it for a considerable time. The precipitate of sulphuret of lead was then filtered off, well washed, and put whilst still moist into a beaker; potash was then poured over it, the fluid heated to 104°–122° F., and a current of chlorine gas passed into it so as to convert the sulphuret of lead into peroxide (PbO^2). This was then determined with protochloride of tin and bichromate of potash, in the way formerly described by me*. The sulphuret of antimony was separated from the fluid filtered from the sulphuret of lead, and after standing for a long time at a moderate heat, it was filtered, and transferred on the filter without washing to a beaker; when it was determined in the manner above described. I obtained the following result:—

Pb	=	83.65
Sb	=	15.11
Cu	}	0.43 (separately determined)
Fe		
Zn		
		99.19

* Chem. Gaz., 1854, p. 269.

By a distinct determination of the antimony I obtained 16.01 per cent.

Determination of Antimony when Arsenic is present.

After ascertaining that antimony could be readily determined by means of protochloride of tin and bichromate of potash, it occurred to me that arsenic would exhibit a similar behaviour. Several experiments, however, made with reference to this point, showed that the two last atoms of oxygen in arsenic acid are more fixedly combined than in antimonious acid; and that it was only by continued boiling of arsenic acid with a concentrated solution of protochloride of tin, that a reduction of this acid, partly into arsenious acid and partly to metallic arsenic, can be effected. The following were the experiments made:—

1. 0.4 gr. of arsenious acid was dissolved in muriatic acid and water, and oxidized to arsenic acid by means of chlorate of potash; the free chlorine was evaporated at a moderate temperature, and a pipette-charge of dilute solution of protochloride of tin was added at about 104° to 122° F. After the lapse of a few minutes, and the addition of iodide of potassium and starch, a normal chrome solution was added until the formation of iodide of starch; this required 16 cub. centims. KO , 2CrO_3 . The same pipette was then again filled with solution of tin, and the strength of the latter tested; it required 15.8 cub. centims. of the chrome solution. From this it appears that under the circumstances the protochloride of tin had not exerted a reducing action upon the arsenic acid.

2. 0.4 gr. of arsenious acid was converted into arsenic acid in the same manner, and digested for a considerable time at 176° F. with a concentrated solution of protochloride of tin (obtained by dissolving 1 gr. of common tin-foil in muriatic acid). The chrome solution was then added until the solution became blue, for which purpose 79.47 cub. centims. were required, whilst 1 gr. of the same tin-foil took 81.5 cub. centims. of the chrome solution. In this case a certain quantity of the protochloride of tin was oxidized by the arsenic acid, but only so much as corresponded with $81.5 - 79.47 = 2.03$ cub. centims. of the chrome solution, which contained 0.01 gr. in 1 cub. centim. The quantity therefore was very small.

3. 1 gr. of arsenious acid was converted into arsenic acid, and then boiled for a long time with the tin solution; a reduction took place, partly with separation of metallic arsenic, from which however only 20 to 28 per cent. of arsenious acid could be calculated.

From these experiments it appears that arsenic acid in dilute solutions is not reduced by protochloride of tin at a temperature of from 104° to 122° F., and that consequently when arsenic and antimony occur together in a fluid, the antimony may be determined by protochloride of tin and bichromate of potash, without any injurious effect from the arsenic, always supposing that dilute solutions are operated with.

The following experiment shows that antimony may very easily be determined in the presence of arsenic. Tartrate of potash and anti-

mony and arsenious acid were oxidized by chlorate of potash, and after the removal of the chlorine, diluted with boiling water at a temperature of 122° F. A measured quantity of a normal solution of tin was then added, the whole was left standing for five or ten minutes with exclusion of air, and the quantity of antimony ascertained by the determination of the excess of the tin solution:—

I.		II.	
A = 0.3 gr. of tartrate		A = 0.3 gr. of tartrate	
dried at 212° F. + 0.2 — 0.3 gr. AsO ³ .		dried at 212° F. + 0.2 — 0.3 gr. AsO ³ .	
G	= 1	G	= 1
K	= 4.37	K	= 2.1
C	= 13.17	C	= 10.9
c	= 0.01	c	= 0.01
Calculated.		Found.	
Per-centage amount of SbO ³			
in the tartar emetic.		I.	II.
46.06		45.31	45.31

The reason why the amount of antimony found in all these experiments is a little too low, is either that the tartar emetic was not perfectly pure, or that a little chloride of antimony is volatilized during the evaporation of the free chlorine. Nevertheless the result is so exact, that it may set aside the ordinary analyses, which are very tedious and generally indirect.

In his paper already referred to, Mohr has given a mode of determining arsenic by dissolving arsenious acid in carbonate of soda, adding a solution of starch, and converting it into arsenic acid by means of a normal solution of iodine. The completion of the reaction is known by the production of iodide of starch. This mode of analysis is excellent, and I hoped to have been able to employ it in combination with my method of determining antimony in analysing a mixture of arsenic and antimony, thinking that oxide of antimony would not decolorize iodide of starch in an alkaline fluid, and would therefore not have an injurious action upon the determination of arsenic. But oxide of antimony, which is partially soluble in an excess of carbonate of soda, behaves in this case exactly like arsenious acid; that is to say, if starch-paste be added to it and a solution of iodine be dropped in, the blue iodide of starch does not make its appearance until all the oxide of antimony in the solution is converted into antimonie acid. Consequently if it were possible to dissolve the whole of the oxide of antimony in a great excess of carbonate of soda, a mixture of arsenic and antimony might be analysed by determining the two bodies together by Mohr's method, and then the antimony alone by mine; the arsenic might then be calculated from the two analyses.

I must take this opportunity of saying something about Dr. Mohr's stopcock burette. This is an admirable instrument, which answers all the requirements of a burette. It possesses two great advantages over Gay-Lussac's burette,—in the first place, a previously deter-

mined quantity of a fluid can be allowed to flow from it, without the least fear of exceeding the proper point; and in the second, it may be very easily made.—Poggendorff's *Annalen*, xciv. p. 499.

On a method of testing the Commercial Archil for its Purity and its Value in Dyeing.* By F. LEESHING, Esq.

The adulteration of the liquid archil of commerce with cheaper articles, especially with logwood extract, is not only practicable, but is actually practised, as I had occasion to convince myself in examining several casks of archil purchased at different times, when thus the presence of logwood extract could not be considered a mere accidental occurrence.

The test first recommending itself in this instance to the practical dyer, would consist in the dyeing of a "swatch" of calico mordanted for madder-reds or chocolates with the suspected archil; in which case only the logwood extract, when present, is expected to fix upon the mordant. This method may prove however deceptive, as the archil itself does also combine in some measure with the mordant, especially when employed somewhat concentrated, and as moreover the success of the dyeing may depend from the more or less acid or alkaline state of the archil, and other causes.

When the amount of logwood extract contained in the archil is considerable, it will indicate itself already if we add some alum or protochloride of tin, and compare the kind of shade obtained with that of pure archil treated in the same manner. These reactions are however not such as to give decisive proof, though they may serve conjointly with the process about to be described, which has the advantage of indicating not only small quantities of logwood, but also of other wood extracts.

If we put 50 drops of pure archil diluted with 3 oz. of water into a flask, and after having rendered the liquid slightly acid by means of acetic acid, add 50 drops of a freshly prepared solution of protochloride of tin (containing 1 part of "crystals of tin" dissolved in 2 parts of water), and heat the flask on a sand-bath, the liquid will be almost decolorized immediately after reaching the boiling-point, exhibiting now only a sallow yellowish tint, with a sediment of the same colour after standing.

A drop of logwood extract dissolved in 3 oz. of water, treated in the same manner, will produce a distinct violet shade, remaining unchanged after several hours' boiling.

Now although this logwood-violet is somewhat modified when mixed with a large proportion of archil, I found it nevertheless easily distinguishable, when an amount of logwood extract of 3 or 4 per cent. at 5° Tw. had been added, by imparting to the boiled liquid a permanent grayish tint. Should the adulteration consist of lima-wood or sapan-wood extract, the boiled mixture would in such a case preserve a red tint. By standing in contact with the air, and by the

* Communicated by the Author.

addition of alkali, the colour of the archil gradually returns again; and whilst thus the colouring principle of archil is reduced and decolorized by an acid solution of protochloride of tin, returning by the addition of alkali and the access of air, I found, on the contrary, the colouring principle of logwood to be reduced by an alkaline solution of tin only, returning by an addition of acid.

In regard to the estimation of the relative amount of colouring matter in different samples of archil, after the absence of wood extracts had been ascertained, it will scarcely be necessary to remark, that neither the deoxidizing property of protochloride of tin nor the bleaching action of chloride of lime could be made use of for this purpose, when we consider the nature of archil manufacture, and the variety of ingredients employed.

I have however besides to mention another fact, which would render such a proceeding quite fallacious. The distinction frequently made by manufacturers betwixt a "blue" and a "red" archil may appear at first sight to be merely owing to the greater amount of alkali in the former than in the latter. This is not however the case, since the red archil (such as came under my examination) could not be converted into the blue one by any additional quantity of alkali. Moreover, in acidifying a pure blue archil and a red archil with equal quantities of acetic acid, and employing them separately for dyeing a certain quantity of wool, the latter was found to yield a dull bluish-red, whilst the former gave a scarlet, when the reverse might have been expected. Not being acquainted with the actual proceeding followed in preparing these two sorts of archil, it will suffice to state, that I found the blue archil to acquire all the properties of the red drug by the addition of a small quantity of red prussiate of potash to the former; and there can be little doubt that such an addition is actually made by some manufacturers.

The presence of red prussiate does not interfere with the described mode of testing for wood extracts; and as to the estimation of the relative strength of different archil samples, this will best be effected by means of the colorimeter, or any glass flasks suitable for the comparison of liquids of different depths of colour. We dilute accordingly equal measures of the samples to be examined with equal measures of water, adding to each a few drops of alkali to render the shades equal in kind (and if this is not effected by alkali, a slight addition of red prussiate may be made to the bluer shades). We compare then the depth of colour, and find the relative strength of the different samples from the amount of undiluted archil we have to add, to obtain shades of equal intensity. Having made out the relations, we may verify these moreover by employing the samples (after neutralization with acetic acid) in those proportions for dyeing equal quantities of wool, passing it after dyeing through lime-water, to render the shades as much as possible equal in kind.

Busby, near Glasgow,
May 14, 1855.

THE CHEMICAL GAZETTE.

No. CCCIV.—June 15, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Salts of Cadmium. By CARL VON HAUER.

1. *Sulphate of Cadmium*, $\text{CdO}, \text{SO}^3 + \text{HO}$.—When cadmium or oxide of cadmium is dissolved in an excess of dilute sulphuric acid, and the solution is concentrated by boiling, a salt is obtained, which separates in verrucose crystals. The salt crystallizes immediately on the cooling of the solution, and corresponds in its constitution with the sulphate of cadmium with 1 atom of water obtained by Kühn.

As the solution of the metallic cadmium in sulphuric acid only takes place slowly, even with the aid of heat, it is advisable to add a little nitric acid occasionally, in order to facilitate the oxidation. This salt is also obtained when concentrated sulphuric acid is added to a boiling saturated solution of sulphate of cadmium; it is immediately thrown down in the form of a fine crystalline powder, and may be almost entirely freed from the adherent sulphuric acid by pressing between blotting-paper. The salt, prepared in three different manners, gave the following results on analysis:—

CdO	56.63	56.70	56.56	1 =	64	56.63
SO ³	35.39	35.45	35.54	1	40	35.39
HO	7.97	7.85	7.90	1	9	7.97

The salt does not effloresce in the air. At 212° F. the loss was 7.85 and 7.90 per cent. in two experiments, so that the salt loses the whole of its water of crystallization at this temperature, and leaves dry sulphate of cadmium. At a red heat it loses sulphuric acid, and there remains sesquisulphate of cadmium. 8

2. *Sulphate of Cadmium*, $3(\text{CdO}, \text{SO}^3) + \text{HO}$, was obtained by the spontaneous evaporation of a saturated solution of sulphate of cadmium. The crystals were determined by Rammelsberg, who found that their form was exactly that of Stromeyer's salt, $\text{CdO}, \text{SO}^3 + 4\text{HO}$. This salt is perfectly stable in the air. At 212° F. it loses 11.78 to 11.84 per cent., or nearly 3 atoms of water; it is then perfectly opaque. At a slight red heat the remainder of the water is driven off, without any loss of sulphuric acid; at a stronger red heat half the sulphuric acid is expelled, and there remains sesquisulphate of cadmium. By long-continued calcination a portion of

the remaining sulphuric acid is driven off; the mass is partially fused, and appears brown from the production of free oxide.

The saturated watery solution of sulphate of cadmium boils at $215^{\circ}6$ F. At $73^{\circ}4$ F., 1 part of water dissolves 0.59 part of anhydrous sulphate of cadmium. Its solubility in hot water is not much greater. The author's analyses led to the above formula:—

CdO	49.75	49.68	49.20	3 =	192	50.00
SO ³	31.35	31.27	31.94	3	120	31.25
HO	18.90	19.05	18.86	8	72	18.75

Sulphate of cadmium dissolves in large quantity in concentrated ammonia with evolution of heat. When the solution is diluted with water, a partial precipitation of hydrated oxide of cadmium takes place. The solution of sulphate of cadmium in ammonia is not immediately precipitated by carbonate of ammonia, but this takes place on the application of heat. If the solution in caustic ammonia be evaporated, it becomes covered with a film, and an uncrystallizable mass is deposited, which dissolved but sparingly in water. This takes place during the spontaneous evaporation of the fluid, but then requires a long time. A cold saturated solution of sulphate of cadmium is not precipitated by alcohol. A thick oily fluid settles to the bottom of the vessel, and the supernatant fluid is at first a little turbid, but soon becomes clear; after a time some rather large crystals are formed at the bottom of the vessel, which appeared both from measurement and analysis to be the salt $3(\text{CdO}, \text{SO}^3) + 8\text{HO}$.

3. *Nitrate of Cadmium*, $\text{CdO}, \text{NO}^5 + 4\text{HO}$, is obtained by dissolving carbonate of cadmium in dilute nitric acid, evaporating the solution, and leaving it to cool. As the salt is very soluble, crystallization only takes place when the fluid is much concentrated. It crystallizes, as stated by Stromeyer, in acicular and columnar crystals united in a radiate form. It deliquesces in the air, as stated by Meissner. At 212° F. it melts in its water of crystallization. The analysis of the air-dried salt gave,—

	Stromeyer.	Hauer.			
CdO	42.15	40.78	1 =	64	41.56
NO ⁵	35.78	34.41	1	54	35.07
HO	22.07	24.81	4	36	23.37

4. *Ammonio-chloride of Cadmium*.—According to Croft, dry chloride of cadmium absorbs 3 atoms of ammonia. The compound thus formed, which has the formula $3\text{H}^3\text{N} + \text{CdCl}$, loses ammonia in the air until it becomes inodorous. The loss of ammonia amounts to 2 atoms, so that there remains a compound of the formula $\text{H}^3\text{N} + \text{CdCl}$. A compound similar to this, and also containing only 1 atom of ammonia, may be obtained, according to Croft, by dissolving chloride of cadmium in heated liquid ammonia, and leaving the solution to cool, when the compound is deposited in crystalline grains. The loss of weight on heating was 16.63 per cent. (H^3N).

By the addition of muriatic acid to a solution of chloride of cadmium in ammonia, Schüller obtained a fine crystalline powder, the constitution of which he found to be $3\text{H}^3\text{N} + \text{CdCl}$; he states that this is the same salt that is obtained by the spontaneous evaporation of a solution of chloride of cadmium in ammonia. By this process the author has obtained a salt with only 1 atom of ammonia, which is consequently the same as that described by Croft, a proof that this compound loses 2 atoms of ammonia, just as quickly as that which is produced by passing ammoniacal gas over chloride of calcium. This loss of ammonia must take place during drying. For analysis, the salt was dried between blotting-paper. It gave,—

H^3N	16.15	1	= 17	15.68
Cd	51.64	1	56	51.66
Cl	32.21	1	35.4	32.65

If hot liquid ammonia be employed in the preparation of this compound, a little precipitated hydrated oxide mixes with it during cooling; it is therefore better to mix ammonia with a cold aqueous solution of chloride of cadmium, until the precipitate which is formed at first is again dissolved, leaving the solution to evaporate spontaneously, when crystalline crusts are deposited. It is nearly insoluble in water.

If carbonate of cadmium, or pure or hydrated oxide, be treated with an aqueous solution of muriate of ammonia, they dissolve in considerable quantities, with evolution of ammonia. The filtered solution furnishes crystalline crusts on evaporation, but these differ very considerably in the proportion of chloride of cadmium and muriate of ammonia, according to the length of the reaction. But if one of the above compounds be boiled for a long time with muriate of ammonia, then filtered and left to cool, anhydrous crystallized chloride of cadmium and ammonium is deposited, with the formula $2\text{H}^4\text{N Cl} + \text{CdCl}$.

5. *Chloride of Cadmium and Ammonium*.—Croft has prepared two salts of chloride of cadmium and ammonium, which according to the author have the following formulæ:—

- a. $\text{NH}^4 \text{Cl} + 2\text{CdCl} + \text{HO}$.
- b. $2\text{NH}^4 \text{Cl} + \text{CdCl}$.

6. *Double Chloride of Cadmium and Potassium* forms two salts of exactly similar composition to the two preceding:—

a. *Double Salt*, $\text{KCl} + 2\text{CdCl} + \text{HO}$.—This is produced when equivalents of the two constituents are dissolved together and left to spontaneous evaporation; it forms silky needles united in tufts. The salt is very soluble; when dried over sulphuric acid, it partially loses its water of crystallization, and this is entirely driven off at 212°F .; in either case it becomes opaque. It undergoes no change at the ordinary temperature of a room. When strongly heated, it melts readily, but loses a part of its chlorine, and is then no longer soluble in water. When dissolved in water, it crystallizes again unchanged from the solution. Its analysis gave,—

100.30

K	13.93	1 =	39.2	14.71
Cd	42.55	2	112	42.04
Cl	29.24	3	106.2	39.86
HO	4.58	1	9	3.37

b. The Anhydrous Double Salt, 2KCl + CdCl.—When the salt *a* has been removed from its mother-liquor, the latter furnishes, on further spontaneous evaporation, large limpid crystals, similar to those of nitrate of soda, and constituted according to the formula $2\text{KCl} + \text{CdCl}$. This salt is remarkable for its great facility of crystallization; whilst the corresponding ammoniacal double salt is generally obtained in scalariform groups of dull crystals, the potash-salt shoots out readily on all sides into perfectly formed transparent crystals, with brilliantly shining faces. This salt can be obtained directly only by mixing watery solutions of at least 3 atoms of chloride of potassium with 1 atom of chloride of cadmium, and leaving the mixture to crystallize.

This salt is rather less soluble in water than the preceding. If the aqueous solution be left to spontaneous evaporation, the salt *a* first of all crystallizes again from it. It melts when strongly heated, and then behaves like the preceding potassium-salt. It undergoes no change in the air. The two salts, $2\text{H}^+\text{NCl} + \text{CdCl}$ and $2\text{KCl} + \text{CdCl}$, are isomorphous. The analysis of the potassium-salt gave,—

K	32.72	2 =	78.4	32.58
Cd	23.66	1	56	23.28
Cl	43.62	3	106.2	44.14

7. Chloride of Cadmium and Chloride of Sodium, NaCl + CdCl + 3HO (air-dried).—A solution containing equivalents of chloride of cadmium and chloride of sodium, concentrated by heat, soon deposits this double salt; it consists of small, dull, verrucose crystals, which are constituted according to the above formula, as stated by Croft. When dried at 212°F ., it loses 12.30 per cent. = 2 atoms water; the third atom is only expelled between 302° and 320°F . From this it would appear that the salt has 2 atoms of water of crystallization and 1 atom of constitution water, the latter being more obstinately retained. The salt may consequently be regarded as a hydrated compound of chloride of sodium with muriate of cadmium, the formula of which would be $(\text{NaCl} + \text{CdO} \cdot \text{HCl}) + 2\text{HO}$; and the salt dried at 212°F ., after losing its water of crystallization, would have the formula $\text{NaCl} + \text{CdO} \cdot \text{HCl}$. When heated, it melts, and behaves like the potassium-salts. It undergoes no change in the air.

8. Chloride of Cadmium and Chloride of Barium, BaCl + CdCl + 4HO.—If aqueous solutions of chloride of barium and chloride of cadmium be mixed and left to evaporate spontaneously, a salt is produced when the chloride of barium is in excess, which forms small crystals, is difficult of solution in water, and appears to contain an indeterminate proportion of chloride of cadmium. When this has been removed, the mother-liquor furnishes large well-formed crystals, which are sometimes transparent when small, but lose their

transparency as they grow larger, although their faces exhibit a brilliant lustre. By placing these crystals in fresh saturated liquor, they may be obtained in the course of a few weeks more than an inch in length. When solutions of equivalents of the two salts are mixed, the salt is obtained directly. It is produced in the same way by spontaneous evaporation and by heat. Analysis:—

Ba	29·62	1 =	68·6	29·64
Cd	24·17	1	56	24·20
Cl	30·56	2	70·8	30·59
HO	15·65	4	36	15·56

The salt is perfectly stable in the air, dissolves readily in water, and crystallizes unchanged from the solution. The above analysis is of the air-dried salt. At 212° F. it loses 8·82 per cent., or 2 atoms of water; the other 2 atoms are only expelled at 320° F. It has then a porcelain-like appearance. Judging from this behaviour of the water, the constitution of the salt might be more exactly expressed by the formula $(\text{BaO} \cdot \text{HCl} + \text{HO}) + (\text{CdO} \cdot \text{HCl} + \text{HO})$, as it indicates more distinctly the part which the water plays in it; it is a simple compound of the two well-known hydrates of muriate of baryta and muriate of cadmium. The composition of the salt, dried at 212° F., at which temperature it loses its water of crystallization, is consequently $(\text{BaO} \cdot \text{HCl}) + (\text{CdO} \cdot \text{HCl})$; and when dried at 320° F., when its constitutional water is expelled, $\text{BaCl} + \text{CdCl}$. When heated to redness, it fuses after the loss of water, forming a clear colourless fluid, which on cooling is not crystalline, and has an enamel-like appearance. The fused mass is no longer perfectly soluble in water; it has therefore probably lost a part of its chlorine.

9. *Bromide of Cadmium and Bromide of Potassium* form the same salts as chloride of ammonium and chloride of cadmium, namely,—

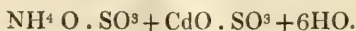
a. $\text{KaBr} + 2\text{CdBr} + \text{HO}$; and

b. $2(\text{KaBr}) + \text{CdBr}$, which is deposited from the mother-liquor of the preceding. They are isomorphous with the above-described chlorides.

The bromide of cadmium employed in the preparation of these two salts was obtained by bringing metallic cadmium in contact with bromine and water. In the distillation of oxide of cadmium with charcoal for the preparation of the metal, the latter is obtained not only in large globules, but also in a finely-divided state, of a grayish colour, very similar to platinum-black. In this form the metal is best fitted for combining with bromine; the combination is effected in a short time and with a considerable evolution of heat. As by this means, even when a large quantity of water is present, a considerable quantity of the bromine is expelled in the form of vapour, it is advisable to bring the two substances in contact in a closed flask, and to put this into cold water if the heat be too great. The solution, which is at first red, soon becomes perfectly colourless, as the combination goes on very rapidly.

10. *Sulphate of Cadmium and Ammonia*.—This salt, which was

first prepared by Mitscherlich, is readily obtained in large well-formed crystals, by the spontaneous evaporation of a solution containing the two salts in equivalent proportions. The crystals undergo no change in the air, and possess a peculiar fatty lustre, and are fatty to the touch; they are only transparent when small, larger crystals being always opaque. The composition of the salt agrees with the general formula of the numerous salts belonging to this series,—



The drying must be very carefully effected, however, to obtain this quantity of water. If large crystals are analysed, without drying them in a pounded state, a considerable quantity more water is obtained than is required by the above formula, even though they should have been long in drying, as they always contain water mechanically, and this is retained very obstinately. Analysis:—

NH ³	7.66	1 = 17	7.59
CdO	28.50	1 64	28.57
SO ³	35.85	2 80	35.71
HO	27.99	7 63	28.12

The salt cannot be dried over sulphuric acid, as it effloresces. When dried at 212°, it loses 26.60 per cent., or 6 atoms of water; the last atom, which is united with the ammonia, is only driven off by a higher temperature, simultaneously with sulphate of ammonia. If the salt be directly exposed to a high temperature, it swells up, and melts partially in the water of crystallization, and the sulphate of ammonia is completely driven off together with the water; sulphuric acid is afterwards expelled, and the residue consists of sesquisulphate of cadmium. The salt may be recrystallized without alteration by dissolving it in a small quantity of water.

11. *Sulphate of Cadmium and Potash*, KO, SO³ + CdO, SO³ + 6HO.—This salt is obtained with difficulty, as the sulphate of potash, which is less soluble, has a greater tendency to crystallize. It is best prepared by saturating a solution of bisulphate of potash with carbonate of cadmium, adding a little sulphuric acid, and leaving the solution to spontaneous evaporation. It could not be obtained pure by concentrating the solution by heat and leaving it to cool. Even the formed crystals are decomposed when the temperature of the mother-liquor changes a little. It is scarcely possible to obtain large crystals in a state of purity, as they are generally covered with small crystals of sulphate of potash. In its crystalline form and constitution the salt resembles the preceding. When the crystals are taken out of the mother-liquor, they exhibit beautifully shining faces, but soon become dull; the efflorescence goes on so rapidly, that it is difficult to get the salt for analysis with its whole 6 atoms of water, unless it is employed with the mother-liquor adhering to it. Analysis:—

KaO	20.23	1 = 47.2	19.25
CdO	26.54	1 64	26.10
SO ³	33.73	2 80	32.62
HO	19.50	6 54	19.50

If the salt has been kept for a few hours in a heated room, only 4 or 5 atoms, or even less water, will be found.

12. *Sulphate of Cadmium and Soda* is obtained by mixing the two salts in equivalent proportions. The crystallization takes place with difficulty, and only when the solution is much concentrated. The salt forms small verrucose crystals, like those of sulphate of cadmium with 1 atom of water. In the air-dried state it contains 2 atoms of water, and is consequently composed according to the formula $\text{NaO} \cdot \text{SO}^3 + \text{CdO} \cdot \text{SO}^3 + 2\text{HO}$. Analysis:—

NaO	16·37	1 =	31	16·06
CdO	32·71	1	64	33·16
SO ³	41·57	2	80	41·45
HO	9·35	2	18	9·32

This salt appears to be obtained with less difficulty when a slight excess of acid is present.—*Sitzungber. der Akad. der Wiss. zu Wien*, xv. p. 23.

On Silicium and Titanium. By H. SAINTE-CLAIRE DEVILLE.

Amongst the compounds of oxygen with simple bodies, there is a group of substances whose analogies are incontestable, and which may be characterized by a single feature in their history. These oxides, which are not acted upon by chlorine alone, become converted into chlorides when in contact with charcoal, under the influence of a current of chlorine at a moderate temperature. Amongst them I shall mention those which will be referred to in this note, namely, silica, titanous acid and boracic acid. The radicals of these generally-diffused substances have not yet been studied in all their details, and I now lay before the Academy the result of my researches upon this subject.

When sodium is treated with chloride or fluoride of silicium in a tray placed in a porcelain tube heated to redness, the last traces of the metal may be removed; and all that is then necessary is to wash the residue, in order to obtain silicium with all the characters attributed to it by Berzelius. But if the portions which do not adhere to the tray be selected, put into a crucible, surrounded and covered with pure fused chloride of sodium, and heated to a sufficiently high temperature for the volatilization of the greater part of the alkaline chloride, two kinds of products are obtained, which vary according to the temperature and the nature of the flux.

In the first place the graphitoid silicium already described by me* as being obtained from the *fonte* of aluminium, may be produced; fused silicium is also obtained in the midst of a gangue which resists the action of heat; it is then frequently crystallized.

Crystallized silicium has much resemblance in colour with specular iron ore when a little iridescent. Its form cannot be exactly

* Chem. Gaz., No. 287, Oct. 2, 1854, p. 362.

measured, the faces of the crystals being always curved; but the form presents so close a resemblance to those of the diamond, that this comparison has been made immediately by all the mineralogists to whom I have shown it. In this state silicium cuts glass.

The analysis of the crystals which accompanied the specimen exhibited furnished the following results:—100 silicium gave 205 of silica; calculation requires 209. The small quantity of matter which was wanting also contained silica and iron, but in proportions which might be neglected. Thus silicium, like carbon, beside which it has been placed in the series of metalloids, is capable of assuming three distinct forms:—

1. The silicium of Berzelius, which represents ordinary carbon.
2. Graphitoid silicium, which corresponds with graphite, and is obtained under the same circumstances as artificial graphite.
3. Crystallized silicium, which is the analogue of the diamond.

Silicium consequently differs from the metals in every respect.

I also exhibit some fused silicium, which has been extracted from different gangues. I cannot however state exactly either the temperature, which was very high, employed in this new experiment, or the mode of preparation which is most proper for attaining a certain result. I must observe only that silicium takes up iron, wherever it exists, even in vessels of common porcelain, which it corrodes in a singular manner*. In preparing silicium, it is necessary therefore to exhaust every precaution in the purification of the original materials, particularly the sodium; to analyse it, it is put with a few drops of nitric acid into a small crucible of Sevres porcelain, and a very small quantity of pure hydrofluoric acid is added (silicium, when strongly heated, resists the action of hydrofluoric acid and nitromuriatic acid); it should dissolve entirely, and the liquid, when evaporated to dryness, should leave no trace of ferruginous matter.

Silicium alloys metals, especially copper, to which it communicates a hardness so great that the metal resists the action of the file. This is copper-steel.

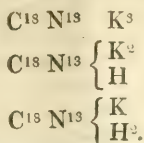
Titanium, obtained by exactly similar processes and calcined in crucibles of alumina, is infusible at a temperature which causes the vaporization of platinum; it resembles very iridescent specular iron ore, and crystallizes in prisms with a square base.—*Comptes Rendus*, April 30, 1855, p. 1034.

On the Mellonides. By J. LIEBIG.

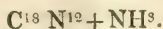
An examination of the mellonides has led me to an incontestable proof that the radical of those compounds contains no trace of hydrogen.

* It reacts upon alumina, at least in the presence of bases, furnishing vitreous products, which appear to me to be new, and which I am at present engaged in analysing. The vessels which I prefer are crucibles of coke, calcined, and immersed whilst still hot in boiling muriatic acid. After remaining for some time in the acid, and being repeatedly washed, these crucibles are very good.

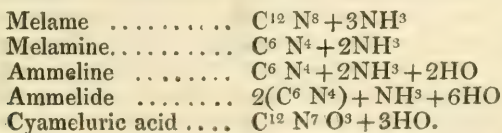
The composition of hydromellonic acid is expressed by the formula $C^{18} N^{13} H^3$. This compound should be a tribasic acid, capable of forming with potassium three distinct compounds, the constitution of which may be expressed by the formulæ,—



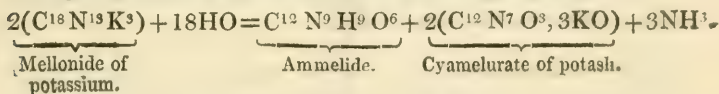
The composition of the mellonide of silver would be expressed by $C^{18} N^{13} Ag^3$. If hydromellonic acid be compared with some compounds of the same group, it may be considered as constituted in the following manner:—



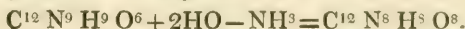
The following products might then be connected with this compound, namely,—



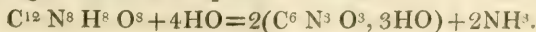
If an excess of potash is set in action upon mellonide of potassium with the assistance of heat, this compound is decomposed by the intervention of 18 molecules of water, forming ammonia, ammelide and cyameluric acid, as shown in the following equation:—



By continuing the action of the potash, the ammelide fixes the elements of 2 molecules of water, and loses 1 molecule of ammonia, becoming converted into the compound, the formation of which, by the action of a proper degree of heat upon urea, has already been signalized by Wöhler and myself. Thus,—



The latter compound is finally converted into cyanuric acid by the prolonged action of the potash. Thus,—



Comptes Rendus, May 7, 1855, p. 1077.

On an easy method of purifying Sulphuric Acid from Arsenic.
By A. BUCHNER.

Arsenious acid is, as is well known, easily changed by the action of hydrochloric acid into the much more volatile chloride of arsenic. If arsenious acid be dissolved in hydrochloric acid, or if a liquid

containing arsenious acid be mixed with hydrochloric acid, and then a sufficient quantity of concentrated sulphuric acid be added, chloride of arsenic, as Liebig has shown, will separate out in oily drops, and as such may be distilled off. Chloride of arsenic boils at 132° , and volatilizes with hydrochloric acid vapour much under its boiling-point, while concentrated sulphuric acid boils at 325° to 327° C.

I am not aware whether these facts have been employed for purifying sulphuric acid from arsenious acid*, but experiments have shown me that they form the basis for such a method of purification. In fact, if sulphuric acid containing arsenic be mixed with a little hydrochloric acid and warmed, or better, if a moderate stream of hydrochloric acid gas be passed through the heated sulphuric acid, all the arsenic is rapidly removed as chloride of arsenic. I have purposely dissolved a large quantity of arsenious acid in sulphuric acid, and then treated it in this manner. In a short time the arsenic was so perfectly removed, that the Marsh's apparatus gave no trace of arsenic even after some time. After passing the hydrochloric acid through, the heat may be continued a short time, in order to drive off every trace of hydrochloric acid, if this be necessary.

I consider this process the only possible one for preparing sulphuric acid pure for chemico-legal investigations. It is known that sulphuric acid cannot be freed from arsenious acid by rectification, because their boiling-points are too near, and because the sulphuric acid is of the two the more volatile; and the precipitation of the arsenious acid out of sulphuric acid by sulphuretted hydrogen is too unpleasant and takes too much time.

This process offers also the advantage, that any nitrous acid which may be present is removed in the form of chloride of nitric oxide.—Liebig's *Annalen*, vol. xciv. 1855.

On the Electrolytic Preparation of the Alkaline and Earthy Metals.
By DR. MATTHIESSEN.

Induced by Bunsen's experiments upon the alkaline and earthy metals, the author has endeavoured to prepare these bodies by electrolysis in Bunsen's laboratory. The treatment of chloride of calcium, chloride of barium, and chloride of strontium between two large plates of charcoal presented peculiar difficulties, which required to be got rid of. These arise from the circumstance, that the metallic granules deposited upon the anode are carried over to the cathode by the currents produced by the evolution of chlorine at the latter. The metals burn at both poles with flame. At the metallic pole oxide is separated from the protochloride, which becomes basic from the action of the moisture of the air; and by this means the current very soon becomes too weak. As Bunsen has found that the decomposition of the chlorides into metal and chlorine depends especially upon the density of the current, particular

* J. Löwe recommended, for the purification of sulphuric acid from arsenious acid, the addition of finely-powdered chloride of sodium to the hot acid. (*Chem. Gaz.* vol. xii. p. 464.)

attention was to be paid to the fulfilment of this condition. By the employment, opposite to the great positive charcoal-pole, of a wire of the thickness of a knitting-needle, the reduction of potassium, sodium, calcium, strontium, &c. took place so easily, that the author regards this experiment as one that may hereafter be performed at lectures. It is however difficult to obtain the separated metals in large globules. For this purpose the author has suggested the three following methods:—

1. The employment of a platinum wire as the positive pole. By this means the metal is alloyed with platinum.

2. Two chlorides are melted together in simple atomic proportions to form a fluid double chloride; the temperature is regulated so that a solid crust is only formed round the negative pole. On cooling, this is found filled with metallic granules.

3. The separation of the metal is effected immediately beneath the surface of the fused chloride, by means of a pole composed of a pointed iron wire. In this way the metal is found swimming on the surface, and adhering to the point of the iron wire. It remains protected by a thin stratum of the fused chloride, which covers it like a varnish, and collects in masses of the size of a mustard seed.

Calcium.—The method here first described is, it must be confessed, uncertain in its results; but in favourable circumstances it furnishes globules of calcium of the size of peas. A mixture of 2 equivalents of chloride of calcium with 1 equivalent of chloride of strontium and muriate of ammonia is melted in a hessian crucible until the last-mentioned salt is volatilized; a cylinder of iron, serving as a positive pole, is then immersed in the fused mixture, together with a narrow clay cell of the length of a finger, previously heated to redness, and filled with the same fused mixture; this serves for the reception of the negative pole, which consists of a piece of iron wire or a stick of charcoal of the thickness of a knitting-needle. When the fused chlorides in the clay-cell stand from $\frac{1}{2}$ an inch to 1 inch higher than in the crucible, the heat of the charcoal-furnace may easily be regulated so that a solid crust shall be formed only in the clay-cell; beneath this the separated metal collects, without coming in contact with the clay-cell. If the current from six charcoal and zinc elements be then allowed to pass through for from half an hour to an hour, a large quantity of reduced calcium is obtained. But in general by this process the calcium is found in a pulverulent form diffused through the mixture of chlorides, which violently decomposes water.

The metal is obtained with more certainty, although in smaller fused globules, by putting the mixture into a small porcelain crucible, such as is used for the calcination of precipitates, heating by charcoal or the spirit-lamp, and passing the current through the mixture by a charcoal pole of as large size as possible, and a piece of iron pianoforte wire (No. 6) not more than 2 lines in length, which is united with the negative pole of the battery by means of a stronger wire reaching close to the surface. A small crust is to be

formed round the wire at the surface. To collect the small globules deposited on the wire, the latter must be taken out about every three minutes, together with the small crust. The globules are crushed in a mortar, and the flattened granules are then picked out.

It may also be obtained in very small granules, but with more difficulty, by just touching the surface of the fused mass of chlorides for a minute or two with the tip of the wire, so that the action of the current produces a sort of appearance of fermentation. The globules are rather larger when the point of the wire is immersed and withdrawn until an electrical flame makes its appearance. By this means an alternate heating and cooling is produced, by which the pulverulent metal is fused together.

Properties of Calcium.—The properties of the metal prepared in the above manner are as follows. Some of them have hitherto not been correctly recognized.

It is a pale yellow metal, of the colour of bell-metal, or of silver alloyed with gold. Freshly-filed spots appear paler and remarkably glittering. Fracture jagged, becoming granular; it is very ductile, and may be cut, bored or filed. A piece of the size of a mustard-seed could be beaten out to a leaf of 10 to 15 millims., and then only showed a few breaks at the margin. In dry air it remains shining, but soon tarnishes in a moist atmosphere. It melts at a red heat on platinum foil, and then burns with a splendid lustre, so that pieces of the quarter of the size of a pin's head give a ball of fire of a cubic inch in size. Calcium filings, thrown into the flame of a spirit-lamp, give beautiful stellate sparks. Dry chlorine has but little action upon it; when heated in chlorine gas, or in vapour of iodine or bromine, it burns with bright incandescence. When thrown upon boiling sulphur, it combines with it, with violent evolution of flame. It combines with vapour of phosphorus, without incandescence, forming phosphuret of calcium. With hot mercury it readily forms a white amalgam. It violently decomposes water, becoming converted into hydrate of lime. Dilute nitric, muriatic, and sulphuric acids facilitate the oxidation; thin laminæ frequently become ignited under the surface of dilute nitric acid; in concentrated nitric acid it retains its bright surface, and is only attacked at a boiling heat. With distilled water as the exciting fluid, it behaves negatively with potassium and sodium, positively with magnesium. It is not however reduced from its chloride by potassium or sodium. —Liebig's *Annalen*, xciii. p. 277.

Note on an Animal Glycogenous Substance. By C. G. LEHMANN.

In a preceding communication, I showed that in fasting-dogs, or dogs nourished exclusively upon meat, there are no traces of sugar in the blood of the *vena porta*, but that there is a considerable quantity in that of the hepatic veins. I have also shown that fibrine disappears in the liver in proportion as the sugar makes its appearance. The latter fact led me, long ago, to express the opinion that the sugar produced in the liver is formed at the expense of the fibrine;

but no one has yet proved chemically that fibrine was a glycogenous substance.

Hæmatine also disappears in considerable quantity in the liver; and I have just discovered a method to show that a glycogenous substance is concealed in the complex product, called hæmatine or hæmatosine. In my investigation of the crystallizable albuminous matter of the blood, I succeeded lately in separating this colouring matter in a state of purity, and obtained fine crystals of it. On carefully submitting this azotized matter to dry distillation, I was surprised to see acid vapours make their appearance at the commencement of its decomposition. It was not until afterwards, when the temperature became more elevated, that ammoniacal vapours were developed.

This appeared to me to prove that hæmatine contains an azotized substance combined with a non-azotized one. All my endeavours to decompose hæmatine so as to produce sugar were without success, except the following. I dissolved hæmatine in alcohol, and added a little nitric acid; the mixture was then boiled, when nitrous æther was formed, and by the production of this nitrous æther (according to Piria's method) the hæmatine loses the whole of its nitrogen. There remained then a non-azotized acid and another substance, which, when dissolved in an alkali, converts deutoxide of copper into protoxide, and which, on the addition of yeast, furnishes carbonic acid and alcohol. From this it seems to me very probable that the hæmatine which disappears in the liver furnishes a part of the sugar which is produced in that organ.—*Comptes Rendus*, April 2, 1855, p. 774.

On the Behaviour of Nitric Acid with Sulphuret of Carbon.

By M. TIFFEREAU.

If 3 vols. of concentrated nitric acid be sealed up in a glass tube with 1 vol. of sulphuret of carbon, so that the mixture occupies one-fifth of the capacity of the tube, nitrous fumes are evolved, and hyponitrous acid is formed. These fumes distil into the upper part of the tube, where they condense into a greenish-blue fluid, which runs down the sides of the tube. Soon afterwards this acquires a green colour with a bluish tinge, and at last it becomes black, the undecomposed nitric acid, which is of a pale colour, lying beneath it.

It requires some weeks before the action of the volatile products of nitric acid upon sulphuret of carbon becomes distinctly perceptible; but then crystals are formed in the upper part of the tube.—*Comptes Rendus*, xxxix. p. 692.

On some Conjugate Ureas. By F. MOLDENHAUER.

Zinin has lately described some compounds produced by treating urea with chloride of benzoyl and chloride of acetyl*. The author

* Chem. Gaz., vol. xii. p. 289.

was engaged in Will's laboratory with similar experiments, which confirm the facts stated by Zinin upon benzoylurea and acetylurea, and prove the existence of a compound containing the radical of butyric and valerianic acids.

Acetylurea, $C^2 \overset{H^3}{C^4} H^3 O_2 \} N^2 O^2$, was obtained by the author by heating equivalents of urea and chloride of acetylene. The mass melts into a tough fluid, which becomes solid on cooling. The solution in hot water or alcohol deposits acicular crystals, which under the microscope are found to be colourless four-sided columns. The compound is unchanged by the air and inodorous; it melts at $233^{\circ}6$ F., forming a tough fluid. At a higher temperature it undergoes the decomposition described by Zinin. Nitric acid and nitrate of mercury do not precipitate this modification. Analysis gave,—

			Calculated.
Carbon	34.97	34.77	35.29
Hydrogen	6.28	6.36	5.88

Butyrylurea, $C^{10} H^{10} N^2 O^4$, is obtained by the treatment of urea with chloride of butyryle; it may be readily recrystallized from water, forming small crystalline scales; from alcohol it separates in thin longish laminae, belonging to the rhombic system. This compound is inodorous and tasteless; it melts at 338° F. to a yellow fluid, which again solidifies in a crystalline form on cooling. It is decomposed by heat in a similar manner to the foregoing compound. Its watery solution is not precipitated by nitric or oxalic acid, or by nitrate of mercury. Analysis gave,—

			Calculated.
Carbon	45.99	46.37	46.15
Hydrogen	8.06	7.99	7.69

Valerylurea, $C^{12} H^{12} N^2 O^4$, is prepared by the action of chloride of valeryle upon urea; it is nearly insoluble in water and alcohol. From the hot aqueous solution microscopic pearly crystals are deposited, which are soft and talc-like to the touch; from alcohol acicular crystals are obtained, which under the microscope are found to be transparent four-sided columns. It melts at $375^{\circ}8$ F., and when carefully heated in a small tube, furnishes a sublimate of broad iridescent laminae. Analysis:—

			Calculated.
Carbon	50.12	49.82	50.00
Hydrogen	8.94	8.64	8.33

Benzoylurea, $C^{16} H^8 N^2 O^4$.—With regard to this compound, the author merely confirms Zinin's statements.

The chloride of valeryle employed in the preparation of the valeryle compound, is a compound which has not hitherto been obtained; the author prepared it by the action of oxychloride of phosphorus upon valerianate of soda. It is a colourless mobile fluid, which fuses when exposed to the air, and is decomposed by water into muriatic and valerianic acids.—Liebig's *Annalen*, xciv. p. 100.

On Nitraniline and Paranitraniline. By A. E. ARPPE.

In his memoir upon the anilides of pyrotartaric acid, the author has described a substance under the name of nitraniline. As further investigations have shown that this substance is very distinct from that described by Muspratt and Hofmann under the same name, the author proposes to call the latter *paranitraniline*. The reason for this change is, that the formation of this substance depends upon a conversion and reduction of nitrobenzole, $C^{12}H^5NO^4$, into aniline; whilst his nitraniline, being produced from a previously existing aniline compound, may bear the latter name with greater propriety. The author has also prepared paranitraniline, and gives the following additional information upon it.

The author prepared paranitraniline according to the process of Hofmann and Muspratt, by treating dinitrobenzole, $C^{12}H^4N^2O^8$, in its alcoholic solution with ammonia and sulphuretted hydrogen; its analysis gave the formula $C^{12}H^6N^2O^4$. It melted and sublimed at $226^{\circ} \cdot 4$ F., depositing in the form of shining laminæ. These are rhombic prisms of 51° and 129° . The crystals are unsymmetrically modified, which is also the case with those deposited from the watery and alcoholic solutions. It is difficult of solution in water, requiring 600 parts at $65^{\circ} \cdot 3$ F. It dissolves much more readily in boiling water, alcohol and æther.

With *muriatic acid* it forms a colourless solution, from which elongated rhombic tables of 120° and 60° are deposited; this muriate dissolves readily in muriatic acid, and is decomposed when dissolved in water, a portion of the base being separated.

Sulphate of Paranitraniline forms shining microscopic crystals, consisting of rhombic prisms, which dissolve in water. The solution has a weak taste, and alkalies precipitate the base from it.

Nitrate of Paranitraniline dissolves readily in water, but with difficulty in nitric acid. When nitric acid is poured over the base, a white powder is formed, which dissolves on the addition of water. Muspratt and Hofmann state, that paranitraniline is violently decomposed by nitric acid, but the author did not find this to be the case.

Tartrate of Paranitraniline forms a yellow solution, from which yellow rectangular crystals are obtained. Potash throws down the base in the form of a yellow crystalline precipitate, which is insoluble in an excess of the precipitant.

Gallotannic Acid, mixed with potash and added to a solution of muriate of paranitraniline, throws down an abundant, flocculent, and almost slimy precipitate, which is decomposed by an excess of potash, when the base is separated in a crystalline form.

Nitraniline.—The author obtained this body, as described in his former memoir, by boiling pyrotartanile, or its corresponding acid, with a dilute solution of carbonate of soda. He has since found that the conversion takes place much more rapidly when a little caustic soda is added to the solution.

When the solution is slowly evaporated, the pure nitraniline shoots into long needles. When it is more quickly cooled, the nitraniline

is obtained in small tabular or acicular crystals of 69° and 111° , in which the smaller angle is truncated so as to produce a six-sided table of 111° and 138° . From the alcoholic solution, rhombic tables are obtained with these six-sided tables; from æther, partly capillary needles, partly prisms; from carbonate of soda, prisms of 55° and 125° ; and when sublimed, partly needles and partly irregular laminæ.

From a new determination, the melting-point of nitraniline is about 286° F., at which temperature it is also volatilized. It sublimes very beautifully between two watch-glasses. It dissolves readily in alcohol and æther, and requires 45 parts of boiling water and 1250 parts of cold water ($65^\circ\cdot3$ F.). Analysis led to the formula $C^{12}H^6N^2O^4$.

Muriate of Nitraniline, $C^{12}H^6N^2O^4, HCl$.—With boiling muriatic acid, nitraniline gives a yellow solution, which becomes colourless when the acid is in great excess, and from which large tabular crystals are produced on cooling. The simplest forms are quadrangular tables of (a) 95° and 85° , and (b) 65° and 115° . By combination of the two, in which the acute angles of (a) are truncated by (b), six-sided tables are produced; the truncation of all the angles (a) furnishes eight-sided tables.

The salt is decomposed by heat, losing a little acid and becoming yellow. The base is almost entirely separated from the acid by water. Alkalies also precipitate it from the solution in water, but the base dissolves again in an excess of the precipitant. Analysis gave 20·20 per cent. of chlorine (calculated, 20·34 per cent.).

Chloride of Platinum and Nitraniline, $C^{12}H^6N^2O^4, HCl + PtCl_2$, with 28·22 per cent. of platinum (calculated, 28·72), was obtained by mixing a concentrated aqueous or alcoholic solution of chloride of platinum with a hot concentrated solution of nitraniline in muriatic acid. The precipitate was washed with a solution of nitraniline in alcohol, and afterwards with æther. The mother-liquor may also be got rid of by pressure. When dried, the salt is of a yellow colour; it dissolves in alcohol, and water precipitates it unchanged, as it is much more difficult of solution in water than in alcohol. From its alcoholic solution it very soon shoots into capillary needles, grouped in a stellate form. It may be heated considerably above 212° F. without decomposition. When more strongly heated, it burns with a faint detonation. Its aqueous solution is decomposed during evaporation; its alcoholic solution is more stable.

When this normal salt is washed with a mixture of alcohol and æther, another compound, of the formula $C^{12}H^6N^2O^4, HCl + 2PtCl_2$, is produced.

Alkalies dissolve a portion of this salt with a red colour, when a bright red powder remains as a residue; this is soluble in water and alcohol, with a bright red colour.

Sulphate of Nitraniline, $C^{12}H^6N^2O^4 + 2SO^3HO$, is obtained by dissolving nitraniline in dilute sulphuric acid, and evaporating it at a gentle heat; it forms large shining laminæ. Small crystals have the form of square prisms under the microscope. The salt has a

strongly acid taste, is decomposed by water, and remains unchanged in the air. It was found to contain 34.41 per cent. of sulphuric acid (calculated, 33.90).

Nitrate of Nitraniline crystallizes in shining needles, cut off at right angles, and of several lines in length; it is decomposed by water.

Oxalate of Nitraniline forms a yellow solution, which deposits yellow needles. It is not precipitated by potash, but dissolves in it with a red colour.

With *gallotannic acid* it behaves like paranitraniline.

The following are additional distinctions between paranitraniline and nitraniline. The former has a pungent, sweet taste, and both in the dry state and in solution, a stronger yellow colour than the latter, which is also nearly tasteless. The acicular crystals of pure paranitraniline are very shining and flexible; nitraniline is less shining, and brittle, so that it is more readily pulverized.—Liebig's *Annalen*, xciii. p. 357.

ANALYTICAL CHEMISTRY.

On the Separation of Cobalt from Nickel.

By T. H. HENRY, F.R.S.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

DEAR SIR,—In the 65th volume of the '*Annalen der Chemie**,' Liebig has described an improved process for the separation of nickel from cobalt, in which he employs prussic acid and potash, instead of the commercial cyanide of potassium, as formerly. As the employment of prussic acid always causes me a headache, I continued to use the method of Rose, described in the 5th volume of the '*Chemical Gazette*,' p. 362, using bromine instead of the chlorine; and I found, by maintaining the temperature at 120° F., that the whole of the nickel was separated in a few hours, free from every trace of cobalt; nor was it necessary to dilute the solution to the extent prescribed by Rose. Latterly, however, I have very carefully tested the method of Liebig, and I find, that in ease and rapidity of execution it may be made to surpass any yet recommended.

It is only necessary to fuse the commercial cyanide of potassium for a few minutes with a little pure charcoal, and when cold to dissolve it in water, and use this solution instead of the prussic acid and potash, or pure cyanide of potassium, which is difficult to prepare and to keep without decomposition.

I had prepared and carefully analysed, some time ago, a con-

* *Chem. Gaz.*, 1848, vol. vi. p. 145.

siderable quantity of the cobalticyanide and nickelocyanide of potassium*. The following were the results obtained:—

		Found.	Calculated.
Co ² Cy ³ + KCy	K	35.20	35.30
	Co.....	17.80	17.74
	C	21.80	21.66
	N	25.67	25.30
		100.47	100.00
KCy + NiCy (dry) .	K	32.11	32.48
	Ni.....	24.46	24.44
	C	19.81	19.88
	N	23.62	23.20
		100.00	100.00

The nitrogen was determined by volume. 11.53 grs. of dry nickelocyanide and 6.86 of the cobalticyanide were dissolved together in water, an excess of the solution of the cyanide of potassium (procured as above) added, the whole boiled, oxide of mercury added; the precipitate, washed, dried and ignited, gave NiO 3.6 = 2.832 Ni, or

24.56 per cent.; theory 24.44 per cent.

Afterwards the solution was neutralized by nitric acid, and the cobalt precipitated by protonitrate of mercury, as suggested by Wöhler; the precipitate, ignited and reduced by hydrogen, weighed 1.20 = 17.49 per cent.; theory = 17.74. Not a trace of cobalt could be discovered in the oxide of nickel by means of the blowpipe.

This experiment has since been amply confirmed by precipitating the two oxides together in the state of hydrate, redissolving them in the above impure cyanide, and proceeding as before; and I believe the process to be one of the most elegant, accurate, and expeditious in the whole range of analytical chemistry.

I remain, dear Sir,

Yours very truly,

T. H. HENRY.

PATENTS.

Patent granted to MM. de Ruolz and de Fontenay, for an improved Metallic Alloy.

THIS invention consists in the production of an alloy, which may be employed for almost all purposes to which silver is usually applied. The improved alloy is composed only of silver, copper and purified nickel; which metals may be combined in any suitable proportions, but the following are preferred:—Silver, 20 parts; nickel, from 25 to 31 parts; and the rest up to 100 parts in copper.

* A portion of this nickelocyanide of potassium was obtained by fusing spongy metallic nickel with animal charcoal and potash.

An alloy is thus produced containing 20 per cent., or thereabouts, of silver, and constituting silver of the third degree of fineness; thus reversing the proportions of the ordinary composition of the second degree, this latter containing 800 parts of silver and 200 of alloy, whereas the improved compound contains 200 parts of silver and 800 of alloy.

The copper employed must be the purest obtainable in commerce, and the nickel should be purified by some suitable process. The means preferred for the purification of the nickel are as follows:—When treating impure nickel of commerce, the metal is to be dissolved in a mixture of hydrochloric and nitric acids, or in dilute sulphuric acid. In the latter case the dissolution must be expedited by electric or galvanic agency, and the operation should be carried on in vessels of platinum. The solution is then submitted to the action of a current of chlorine, and the iron impurities precipitated therefrom by boiling with carbonate of lime, care being taken not to have too great an excess of this latter substance.

The nickel is then precipitated by carbonate of soda, and taken up again by hydrochloric acid, and diluted with a large quantity of water. The solution is then saturated with chlorine gas, and an excess of carbonate of baryta is added thereto. The liquor must then be left in repose in a cold state; and the nickel may either be precipitated in the metallic state by means of a galvanic current, or precipitated in the form of an oxide; which oxide may be afterwards reduced to the metallic state in the ordinary manner.

When treating spess, take of this substance 100 parts; nitre, 20 parts; and felspar, 100 parts. By this means cobalt is produced in the state of blue glass. This is to be roasted and washed, and dissolved in sulphuric acid. The remainder of the process is to be effected in the manner above described for the treatment of impure nickel.

Although the proportions above given are those generally employed for the production of the improved alloy, the proportion of silver may be variously increased up to the following limit, viz. silver, 30 parts; nickel, 31 parts; and copper, 49 parts; total, 110 parts.

It is advantageous, first, to melt the copper and nickel in the granular state, and afterwards to introduce the silver; and the flux to be employed in this case consists of charcoal and borax, both in the state of powder; and the ingots obtained are to be rendered malleable by annealing for a considerable time in powdered charcoal.—Dated December 30, 1853.

Patent granted to MM. de Ruolz and de Fontenay, for Improvements in the Treatment of certain Metals for producing an improved Metallic Alloy.

These improvements consist principally in additions to, and modifications in, the process before described.

It has been found by experiment, first, that this new combination of metals can be so far advantageously modified as to employ the

following proportions, viz. copper as high as 49 parts, nickel 31, and silver from 20 to 40, making a total of 100 to 120. Second, that phosphorus can be usefully introduced into these alloys, and in certain cases extracted after the required effect has been produced by it.

The nickel and copper are first melted, then brought into a granular state, and are afterwards replaced in the crucible and remelted, after which the silver is added. The best flux which can be used is an intimate mixture of borax and powdered charcoal. The ingots, when obtained, must be slowly annealed at a cherry-red heat, in a closed vessel, with powdered charcoal.

As to the use of phosphorus:—1. If it be required to obtain cast articles, such as statuettes and objects of art, a certain quantity of phosphorus must be introduced into the combination. The introduction of phosphorus can be effected in several manners, viz. first, by melting the mixture of the three metals with a mixture of equal parts of acid phosphate of lime and powdered charcoal brought to a red heat; secondly, the mixture of the three metals may also be heated together, with a mixture of 100 parts of phosphate of lime, 50 parts of sand, 75 parts of borax, and 10 parts of charcoal. As regards the relative proportions of the metallic alloy and the phosphorated mixture, described above, the following are the most suitable for cast articles:—1000 parts of the alloy of silver, copper and nickel, and about 150 parts of the phosphorated mixture. The quantity of phosphorus to be added depends upon the length of time taken in heating. Thirdly, the following method is the most preferable. The operation is as follows:—Phosphuret of copper is prepared in the ordinary way, and its richness in phosphorus is ascertained by analysis. This phosphuret of copper is then remelted and granulated, after which the following mixture is melted:—Phosphuret of copper, 49 parts (of such a strength as to be capable of introducing into 100 parts of the alloy from one-thousandth to twenty-thousandths of phosphorus); nickel, 31 parts; and silver from 20 to 40 parts, or more, as desired by consumers. It should be well understood that the silver must not be introduced into the alloy until the phosphuret of copper and the nickel are completely melted and combined or mixed. The effects produced by this introduction of phosphorus are, to augment the fusibility of the alloy; causing it, when melted, to run in a very limpid state, to obtain a closer grain, to avoid all porosity, and to have a greater homogeneity, and finally to render the whiteness greater.

2. In order to preserve the advantages arising from the presence of phosphorus when articles are required to be forged, rolled or stamped, it is necessary, during this operation, to restore the ductility and malleability which the phosphorus has to a great extent impaired. To effect this, after having obtained regular and homogeneous ingots by the aid of the phosphorus, the phosphorus must be almost totally eliminated or abstracted, which may be effected by submitting, during a long time, the metal to a cherry-red heat, in a close vessel, with powdered charcoal.—Dated September 25, 1854.

THE CHEMICAL GAZETTE.

No. CCCV.—July 2, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the action of Aniline on Isatine, Bromisatine and Chlorisatine.

By A. ENGELHARDT.

ANILINE acts upon a solution of isatine in anhydrous alcohol, exactly like dry ammonia. By the action of ammonia upon isatine, Laurent obtained imesatine, $C^{16}H^5NO^4 + NH^3 = C^{15}H^6N^2O^2 + H^2O^2$.

The author has prepared from isatine, bromisatine, and chlorisatine, the compounds of the aniline series corresponding to imesatine; he calls them phenylimesatine, phenylobromimesatine and phenylochlorimesatine. They are produced in accordance with similar equations to the above:—

1. Phenylimesatine, $C^{25}H^{10}N^2O^2 = C^{16}H^5NO^4 + C^{12}H^7N - H^2O^2$.

2. Phenylobromimesatine, $C^{29}H^9BrN^2O^2 = C^{16}H^4BrNO^4 + C^{12}H^7N - H^2O^2$.

3. Phenylochlorimesatine, $C^{28}H^9ClN^2O^2 = C^{16}H^4ClNO^4 + C^{12}H^7N - H^2O^2$.

Phenylimesatine, $C^{25}H^{10}N^2O^2$, is obtained by dissolving 7.35 parts of isatine in alcohol, adding 4.65 parts of aniline to this solution, boiling the whole, and leaving it to cool. These quantities furnished 10.5 parts of phenylimesatine, which was purified by recrystallization.

Properties.—It crystallizes from alcohol in shining, yellow, acicular crystals, grouped in a stellate form; under the lens these are seen to be fine, transparent, acutely-pointed crystals. They dissolve readily in boiling alcohol, but with much more difficulty in this fluid when cold; the solution has an orange-yellow colour. They are extremely difficult of solution in boiling water; the solution is yellow, and on cooling deposits flakes, which consist of fine golden-yellow needles. They are soluble in æther.

When heated on platinum foil, it melts at first to a dark red fluid, which on cooling forms an amorphous mass. If further heated, it is decomposed, leaving a bulky cinder, and evolving a yellow vapour, which acts disagreeably upon the respiratory organs. The addition of muriatic acid to the alcoholic solution of phenylimesatine produces a red colour when the mixture is boiled; on the cooling of this solution, isatine is deposited in the form of flat red prisms, and muriate of aniline remains in solution.

Chem. Gaz. 1855.

It dissolves with the assistance of heat in nitric acid, without evolution of reddish-brown fumes; the solution is red. It dissolves in strong sulphuric acid, forming a dark red fluid, which when diluted with water acquires a yellow colour.

When heated with a strong aqueous solution of potash, it first of all acquires a dark red colour, but is afterwards decomposed, depositing aniline and forming a yellow solution (of isatinat of potash). The solution is rendered brown by the addition of muriatic acid, and when evaporated and cooled furnishes isatine.

The analysis of phenylimesatine gave,—

C	76.04	28	=	168	75.67
H	5.09	10		10	4.51
N	12.96	2		28	12.61
O	..	2		16	7.21

Phenylbromimesatine, $C^{28}H^9BrN^2O^2$.—This is obtained by dissolving 4.52 parts of bromisatine in boiling alcohol, adding 1.86 part of aniline, boiling and evaporating. It is purified by recrystallization.

Properties.—Crystallized from alcohol, it forms beautiful, orange-yellow, silky, flat needles, which dissolve very readily in boiling alcohol, but are less soluble in that fluid when cold; they are nearly insoluble in boiling water, although the water acquires a faint yellow colour.

The alcoholic solution of phenylbromimesatine, treated with boiling muriatic acid, acquires a red colour, and is decomposed into bromisatine, which is deposited on the cooling of the solution, and aniline, which remains in solution in the form of muriate.

When heated with an aqueous solution of potash, phenylbromimesatine first of all becomes dark red, and is afterwards decomposed, depositing aniline, and forming a yellow solution (of bromisatinat of potash), which when heated with muriatic acid acquires a red colour and deposits bromisatine. Analysis gave 56.42 per cent. of carbon and 3.54 per cent. of hydrogen, agreeing with the above formula.

Phenylchlorimesatine, $C^{28}H^9ClN^2O^2$.—For the preparation of this compound, 3.5 grms. of chlorisatine were dissolved in boiling alcohol of 0.833 spec. grav., 2.5 grms. of aniline were added to this solution, which was then heated, a little evaporated and set to cool. Reddish-brown, sharp-pointed, flat prisms were then deposited from the fluid; they were grouped in bundles.

Properties.—Phenylchlorimesatine dissolves very readily in boiling alcohol, and also pretty well in cold. When the alcoholic solution is strongly and suddenly cooled, it crystallizes in orange-yellow needles, which so closely resemble the needles of phenylbromimesatine, that it is difficult to distinguish them. When its alcoholic solution is slowly cooled, it crystallizes in flat, pointed, reddish-brown prisms. It is very difficult of solution in water, but communicates a yellowish colour to that fluid. Its alcoholic solution is decomposed by muriatic acid into chlorisatine and aniline. When heated

with a watery solution of potash, aniline is set free, and a yellow solution (of chlorisatinat of potash) is formed; this, when heated with muriatic acid, becomes red, and chlorisatin is separated. Analysis gave,—

C	66.07	28 =	168	65.50
H	3.95	9	9	3.51
Cl	..	1	35.5	13.84
N	..	2	28	10.91
O	..	2	16	6.24

The author also endeavoured to combine isatine with nitraniline and tribromaniline, but without success. He also tried the effects of chloride of benzoyle upon imesatine, and found that when heated, muriatic acid is evolved, and that the residue, when treated with potash, had the odour of benzonitrile and the appearance of a brown resinous mass.

Whilst observing the action of chloride of benzoyle upon isatine, he remarked, that on the application of a gentle heat, the isatine dissolved in the chloride of benzoyle, and crystallized from it on cooling unchanged, but when strongly heated, a decomposition took place, by which a black carbonaceous mass was formed; on one occasion he even obtained a dark blue crystalline powder, which was scarcely soluble in alcohol.—*Bulletin de St. Pétersb. Class. Phys. Math.*, xiii. p. 357.

On the Preparation of pure Crystallized Sulphuret of Tin.

By R. SCHNEIDER.

The preparation of sulphuret of tin by the direct fusion of tin and sulphur is attended with difficulty, as a portion of the sulphur is always volatilized at the temperature at which the two substances combine; and it is only by the repeated fusion of the mass first obtained with sulphur, that sulphuret of tin of nearly normal composition can be procured.

Pure crystallized sulphuret of tin may however be prepared by adding this substance, as obtained by precipitation from solutions of oxide of tin with sulphuretted hydrogen gas, and drying, in small quantities to fusing anhydrous protochloride of tin, as long as any of it is taken up. The solution thus produced has a fine dark brown colour whilst heated. During the cooling the sulphuret of tin crystallizes from it in abundance in small laminæ. These may be readily separated from the mass of chloride of tin in which they are imbedded, by treating the latter with very dilute muriatic acid. A blackish-brown powder, which is separated at the same time (probably the same substance in an amorphous state), may easily be separated from the larger crystalline laminæ by suspension in water. The laminæ are then washed with muriatic acid, and lastly with pure water.

The sulphuret of tin thus obtained forms small crystalline laminæ, which have a dark lead-gray colour and a brilliant metallic lustre; they are fatty and mica-like to the touch, and can only be triturated

with difficulty, when they form a dark blackish-brown powder. Their specific gravity is 4.973. Karsten found the specific gravity of sulphuret of tin to be 4.852, and Boullay 5.267.

The compound is only attacked slowly and with difficulty by nitric acid, even when boiling; a little stannic acid is separated. Boiling muriatic acid, on the contrary, decomposes it readily and completely, with evolution of sulphuretted hydrogen.

In analysis, 1.588 grm., moistened with a few drops of nitric acid, and carefully roasted and calcined, gave exactly 1.588 grm. of stannic acid. As the equivalents of stannic acid and sulphuret of tin are the same, these numbers show that the substance under investigation is constituted exactly according to the formula SnS .—Poggendorff's *Annalen*, May 1855, vol. xcv. p. 169.

On some new Bodies of the Propylenyle Series. By N. ZININ.

Propylenyle behaves in its combinations exactly like æthyle. Iodide of propylenyle resembles a compound corresponding to hydriodic acid, and its alcoholic solution even acts, although slowly, upon salts of potash. But if it be brought in contact with silver salts, the mixture soon becomes strongly heated, the silver is converted into iodide of silver, and neutral bodies are formed, which contain the propylenyle as well as the acid of the silver-salt employed. The reaction is very precise; and if a sufficient quantity of the silver-salt be employed, the quantity of the body obtained always exactly corresponds with that of the iodide of propylenyle employed.

Well-dried pure acetate of silver was put into a retort with nearly its equivalent of iodide of propylenyle (a slight excess of the silver-salt was generally used), and the mixture was well stirred with a glass rod; the action commenced in a few minutes, and when the quantity of the two substances employed was not too small (at least 4 grms. of each), and the retort was about half-filled with them, the heat produced was sufficient to distil over nearly the whole of the aceto-propylenyle. A little iodide of propylenyle passes over at the same time; and the best mode of preventing this, is to arrange the apparatus in such a manner that the portion volatilized during the reaction shall condense upon the sides and in the neck of the retort, and flow back upon the saline mass. To obtain the whole of the volatile product formed, the retort is afterwards placed as deeply as possible in a chloride of zinc or oil-bath, and gradually heated from 212° to 230° or 302° F. The weight of the entire apparatus before and after the experiment remains the same, so that no gaseous products are formed, and the quantity of aceto-propylenyle obtained corresponds with that of the iodide of propylenyle employed.

The fluid obtained is distilled again, first over a small quantity of acetate of silver, in order to decompose any possible residue of iodide of propylenyle; it is then distilled over oxide of lead, and lastly by itself, when nearly all passes over at 302° F. This temperature, at which pure aceto-propylenyle always boils, exceeds the boiling-point of aceto-æthyle, in about the same proportion,

as the boiling-point of iodide of propylenyle that of iodide of æthyle. Aceto-propylenyle is lighter than water, and dissolves in it very sparingly; it mixes with alcohol and æther in all proportions. It has a neutral reaction; its odour resembles that of acetic æther, but is rather sharp, and it has a pungent ætherial taste.

Its analysis gave 59.66 per cent. of carbon and 8.21 of hydrogen, agreeing with the formula $C^4 H^3 (C^6 H^5) O^+$.

Iodide of propylenyle acts upon dry crystallized benzoate of silver; but in this case, in order to distil over the whole of the volatile product, the heat must be raised after the reaction to $482^\circ F$. No gaseous products are formed, either during the reaction or in the subsequent distillation, for the weight of the apparatus is the same both before and after the experiment. The quantity of the product obtained corresponds with that of the iodide of propylenyle employed.

The fluid obtained is distilled again with a small quantity of benzoate of silver, then washed with carbonate of soda, and dried by means of chloride of calcium; it is then distilled first over oxide of lead, and afterwards by itself, when nearly the whole passes over at $467^\circ.6 F$. This is the boiling-point of benzopropylenyle, which is also about $54^\circ F$. higher than that of benzoic æther. Benzopropylenyle is an oleaginous fluid, heavier than water, in which it is insoluble; it mixes with alcohol and æther in all proportions, has a neutral reaction, and an odour like that of benzoic æther. Its analysis gave 74.29 carbon and 6.44 hydrogen, agreeing with the formula $C^{14} H^5 (C^6 H^5) O^+$.

By the action of iodide of propylenyle upon carbonate of silver, an oleaginous ætherial fluid is obtained, which is lighter than water and is insoluble in that fluid.

In contact with caustic potash, either dry or in its concentrated aqueous solution, the two compounds above described become heated and decomposed; this takes place with benzopropylenyle more readily than with acetopropylenyle. By careful distillation with a slight excess of potash, a residue is obtained consisting of perfectly white potash salts of the corresponding acids; and the distillate from both bodies is the same volatile fluid, which mixes with water in all proportions, and has a faint odour, which however strongly affects the eyes and lungs.

Iodide of propylenyle (containing a little dissolved iodine) combines with mercury much more quickly than iodide of methyle or iodide of æthyle. The mixture, when shaken, is very soon converted into a crystalline yellow mass, from which hot alcohol and æther readily extract the newly-formed compound, iodide of hydrargyropropylenyle. When the dry mass is extracted with alcohol, silvery scales are obtained on cooling, and these, as they are very sparingly soluble in cold alcohol, cause the whole fluid to set. This body is almost entirely insoluble in water; when exposed to the light, especially during drying, it acquires a yellowish colour, but retains its metallic lustre, and undergoes no loss of weight. When heated to $212^\circ F$., it is volatilized in the form of white, shining, rhombic

prisms; at 275° F. it melts, and on cooling forms a yellow crystalline mass. When more strongly and rapidly heated, it is for the most part decomposed, and furnishes a yellow sublimate, leaving behind a carbonaceous residue; alcohol extracts a little undecomposed matter from the sublimate.

When an alcoholic solution of this body is mixed with a solution of nitrate of silver, the whole of its iodine is separated as iodide of silver. Oxide of silver, digested with an alcoholic solution of the body, is also converted into iodide of silver; the fluid acquires a strongly alkaline reaction, and when evaporated gives a thick, syrupous, strongly alkaline mass, which is soluble in water, and when further heated is volatilized, diffusing an odour resembling that of angelica and garlic. With acids this mass furnishes salts, which are soluble in alcohol and water; the sulphate is not very soluble in alcohol, and is deposited therefrom in the form of a white powder, composed of microscopic scales, grouped in a globular form. Its analysis gave 34.49 iodine, 9.59 carbon, and 1.38 hydrogen, agreeing with the formula $C^6 H^5 Hg^2 I$.

There is no doubt that the body produced by the action of oxide of silver upon iodide of hydrargyropropylene, corresponds both in its composition and properties with the oxide of hydrargyræthyle, and that it is oxide of hydrargyropropyle, so that in this respect the group $C^6 H^5$ behaves in an analogous manner to the æthyle groups. — *Bulletin de St. Pétersb. Cl. Phys. Math.*, xiii. p. 360.

On the Preparation of Ferrum pulveratum. By Prof. WÖHLER.

Medical experience has shown that metallic iron, in a finely divided state, is more efficient than any of the compounds of this metal which have been used. Formerly mechanically powdered bar iron was employed under the name of *ferrum pulveratum*, until in 1840 Quevenne and Miquelard* proposed to obtain it by reducing the oxide by hydrogen. Iron obtained in this manner perfectly pure, appears to have essential advantages over the ordinary, less soluble and carbonaceous bar-iron powder. It is now generally used in France under the name of *fer réduit*.

The mode of preparation is very easy, and may be conducted by any druggist. The most troublesome part is the preparation of pure oxide of iron, if this is done by precipitation by ammonia. It is better to adopt the following process, recommended by Faraday, for the preparation of polishing powder:—Pure crystals of sulphate of iron are heated in an iron pan until perfectly dehydrated, the powder mixed with twice or three times its weight of pure dry chloride of sodium, introduced into a clay crucible, and heated to redness until it melts. When the melted mass is cold, it is washed with water, and the oxide of iron remains as a crystalline powder of a blackish-red colour.

The oxide of iron thus obtained is reduced by ignition to redness

* Mémoire sur l'Action Physiologique et Thérapeutique des Ferrugineux. Par Quevenne, in the Archives de Physiologie, sous la Direction de Bouchardat No. 2, October, 1854.

in a current of dry hydrogen, either in a glass tube or gun-barrel. The gas is generated from iron and sulphuric acid, and care must be taken that the latter is not arsenical. The gas is dried either by sulphuric acid or chloride of calcium, introduced between the generator and the tube containing the oxide.

As soon as atmospheric air is displaced from the apparatus, the tube is heated to full redness, and the temperature and current of hydrogen maintained so long as the formation of water is observed at the open end of the tube. When this is at an end, the tube is removed from the fire, closed at each end, and when cold the reduced iron transferred to a bottle. Care must be taken to prevent access of air to the reduced iron while hot, as it is highly pyrophoric in this state. The reduced iron thus prepared should not appear black in places, which would show that the reduction was imperfect. It should consist of small gray lamellar crystals, of the same form as the oxide of iron. These crystals are porous pseudomorphs, and may therefore be reduced to very fine powder with ease.

When well prepared, the *ferrum pulveratum* should be a light gray powder without lustre. When pressed with a polished substance, it acquires metallic lustre. When heated, it readily burns. It should be perfectly soluble in dilute sulphuric acid, with evolution of hydrogen.—*Ann. der Chem. und Pharm.*, April 1855, and *Pharmaceutical Journal*.

On the Preparation of Hydrated Carbonate of Lime. By J. ROTH.

When to a great excess of a concentrated solution of bicarbonate of soda, is added a concentrated solution of 1 atom of a salt of lime and 1 atom of a salt of magnesia (nitrate or muriate), the voluminous precipitate, the particles of which appeared globular under the microscope in the first instance, is seen gradually to shrink, evolving carbonic acid, and becoming entirely converted into crystals of hydrated carbonate of lime, $\text{CaO} \cdot \text{CO}_2 + 5\text{HO}$. The magnesia at first remains dissolved with a little lime; but after standing some time, needles of hydrated carbonate of magnesia are formed. If the crystalline lime precipitate be quickly filtered, and another atom of the lime-salt be added to the solution, a fresh precipitate of the crystallized hydrated carbonate of lime is produced, and so forth, until the solution becomes rather more diluted, when globules of carbonate of lime make their appearance with it, and these sooner or later become converted into rhombohedra of calc-spar. The temperature of the solutions must not exceed 61°F. ; at this temperature single crystals of the hydrated carbonate of lime are obtained with an excess of the globules of calc-spar. It is a matter of indifference whether the magnesia-salt be added to the solution of bicarbonate of soda before the lime-salt, or mixed with it, and both added at the same time.

If the fluid be filtered immediately after the addition of the salts of lime and magnesia, the precipitate will contain both lime and magnesia; the latter is afterwards redissolved in the soda.

If diluted solutions, or a larger quantity of lime than magnesia, be employed, or if a solution of bicarbonate of soda be added to an excess of the salts of lime and magnesia, only a few crystals of hydrated carbonate of lime are obtained, with a large quantity of calc-spar globules. In the latter case the soda does not at first produce turbidity in the solution of the earthy salts, and the precipitation only commences when a considerable quantity of it has been added.

If carbonic acid be passed into the saturated solution of carbonate of soda, and the solution of lime and magnesia be then added, only a few crystals of hydrated carbonate of lime are obtained, with a large quantity of calc-spar.

The crystals of hydrated carbonate of lime prepared in the above manner are very sharply defined and polyhedral. They are rapidly decomposed, under water, in the air or in the mother-liquor; the decomposition is often seen, under the microscope, to commence with a turbidity in the interior of the crystal. Even when protected from the air by Canada balsam, the crystals are very rapidly decomposed.

No hydrated carbonate of lime could be obtained by a similar process with bicarbonate of potash, but carbonate of lime was always thrown down; subsequently the well-known double salt of bicarbonate of potash with carbonate of magnesia was formed. An attempt to obtain hydrated carbonate of baryta from a solution of baryta and magnesia, was equally unsuccessful.—Poggendorff's *Annalen*, May 1855, vol. xcv. p. 172.

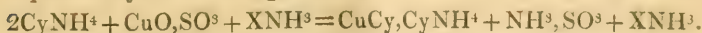
ANALYTICAL CHEMISTRY.

Volumetric Determination of Hydrocyanic Acid and of the Cyanides of the Alkaline Metals. By CARL MOHR.

THE author observes, that although Liebig's method for the determination of the above bodies renders a new process for this purpose less desirable than is the case with many other bodies, the process of volumetric analysis proposed by him may be useful for the purpose of checking the results of Liebig's method.

If a solution of a salt of oxide of copper be added to a fluid containing hydrocyanic acid with an excess of ammonia, the blue colour of the compound of oxide of copper and ammonia disappears until the formation of the compound of equivalent parts of cyanide of copper and ammonium, $\text{CuCy} + \text{CyNH}_4$. Each drop of the solution of copper produces a deep azure-blue spot, which immediately disappears on stirring; and if the operation be carried on in a white porcelain saucer, the slightest tinge of blue may be distinctly recognized. At first the disappearance of the blue colour is instantaneous, but towards the end it takes place more slowly; and the volume employed is only to be noted when the same colour reappears in the fluid after a few moments; it does not afterwards disappear.

With reference to these experiments, the decomposition may be expressed by the following formula:—



From this formula it may be seen, that 1 atom of copper-salt added represents 2 atoms of cyanogen. If therefore a solution of sulphate of copper be prepared containing $\frac{1}{10}$ th of an atom, or 12.468 grms. in the litre, each cubic centimetre will represent $\frac{2}{10000}$ ths of an atom, or 0.0054 grm. of anhydrous hydrocyanic acid.

Hydrocyanic acid of indeterminate strength was prepared by the distillation of prussiate of potash with sulphuric acid. This was tested by a copper solution, a silver solution of exactly the same strength ($\frac{1}{10}$ th of an atom = 10.8 grms. of metallic silver in the litre), and with the copper solution itself. 10 cub. centims. required,—

Silver solution.		Copper solution.	
1.	7.5 cub. centims.	1.	7.6 cub. centims.
2.	7.5 ...	2.	7.5 ...
		3.	7.5 ...

Taking 7.5 as the result of the majority of the experiments, 10 cub. centims. of the hydrocyanic acid tested represented $7.5 \times 0.0054 = 0.0405$ grm. of anhydrous hydrocyanic acid.

A mere glance at the above numbers justifies the conclusion, that in both cases a perfectly homologous cyanide was formed. That the whole of the copper added had entered into combination is proved by the disappearance of the colour, as the blue colour of the compound of oxide of copper and ammonia instantly makes its appearance as soon as more copper than can enter into combination has been added.

To ascertain whether only a single compound is formed in all cases with varying proportions of the copper solution and hydrocyanic acid, the author endeavoured to determine a known quantity of sulphate of copper by means of hydrocyanic acid of known strength. 20 cub. centims. of the normal solution of copper were mixed with an excess of ammonia, and 30 cub. centims. of hydrocyanic acid were poured into it from the burette; the fluid became quite colourless. 10 cub. centims. of this hydrocyanic acid took 7.5 cub. centims. of the copper solution to reproduce the colour. The exact quantity of hydrocyanic acid necessary for decoloration could not be determined directly, as the transition to the colourless state is not so distinctly marked as the opposite phenomenon; the excess of hydrocyanic acid was therefore found by the copper solution; in this case it took 2.4 cub. centims., representing 3.035 cub. centims. of hydrocyanic acid. If this be deducted from the 30 cub. centims., the number of cubic centimetres required for decoloration = 26.965. If these be calculated back for copper solution according to the found proportion, we have,—

Proportion by weight.		Proportion by volume.	
Employed.	Found.	Employed.	Found.
0.24936	0.252	20 cub. centims.	20.213 cub. centims

On a repetition of the experiment, a still closer agreement was obtained.

For further confirmation, another hydrocyanic acid was tested by the two methods; 10 cub. centims. of hydrocyanic acid required,—

By the silver method.	By the copper method.
7 cub. centims.	7.1 cub. centims.
7 ...	7.0 ...
	7.0 ...
20 cub. centims. hydrocyanic acid	14.1 cub. centims.
20 	14.0 ...

10 cub. centims. hydrocyanic acid consequently contain 0.0364 grm. of cyanogen, and 7 cub. centims. of the normal solution of copper 0.02217 grm. of metallic copper. If each of these numbers be divided by the atomic weight of the bodies, the relative number of atoms of each contained in the double compound is obtained, namely,—

0.0007 atoms of copper and
0.0014 atoms of cyanogen.

There are therefore 1 atom of copper and 2 atoms of cyanogen in the compound. All the experiments prove the existence of the compound $\text{CuCy} + \text{NH}^2 \text{Cy}$, and show that no intermediate forms are produced in this process.

A potassium compound corresponding with the ammonium compound exists, but as little is known about it, the author has given the following experiments. The hydrocyanic acid employed was found by several analyses to contain 0.1924 per cent. of cyanogen.

10 cub. centims. of this acid were mixed with an excess of caustic potash, and the normal solution of copper added until the formation of the compound of oxide of copper and potash indicated the conclusion of the reaction :—

10 cub. c. hydrocyanic acid represented 4 cub. c. copper solution.
20 7.9

Consequently 20 cub. centims. of the hydrocyanic acid took on the average 7.95 cub. centims. of the copper solution. Here also calculation shows that there are 2 equivs. of cyanogen to 1 equiv. of copper, and that the simplest expression of the compound is the formula $\text{CuCy} + \text{CyKa}$.

The cyanide of potassium, prepared according to Liebig's method, cannot be determined by this method; the presence of cyanate of potash is probably the cause of error. But if the cyanide of potassium is free from cyanate, the determination may be successfully performed, as has been proved by several analyses.

10 cub. centims. hydrocyanic acid with ammonia required 7 cub. centims. of the solution of copper; with potash and ammonia,—

10 cub. centims. = 6.8 cub. centims. copper solution.
20 ... = 13.9
Tested with ammonia. With ammonia and potash.
0.378 per cent. hydrocyanic acid. 0.370 per cent.

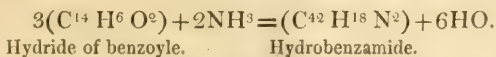
The author's endeavours to obtain the double compound above referred to in a crystalline state were unsuccessful. Concentrated hydrocyanic acid was added to an ammoniacal solution of sulphate of copper until the disappearance of the colour, and the whole was then placed in the cold to crystallize. No crystals were formed in three days, but a distinct odour of cyanogen was perceptible, whilst the ammonia only slightly predominated. When the solution was evaporated at a gentle heat, two salts crystallized from it. A decomposition of the compound had taken place, with evolution of cyanogen, and a double compound, $\text{CuCy} + \text{Cu}^2\text{Cy}$, already described by Dufau, had separated. This, when muriatic acid was poured over it, evolved much hydrocyanic acid. The second salt was regenerated sulphate of copper.

The percyanide of copper does not exist in an uncombined state; it becomes decomposed into protocyanide and cyanogen, and it is only in presence of an excess of alkali that this double compound is formed; if this solution be supersaturated with muriatic acid, white protocyanide of copper is precipitated, with evolution of hydrocyanic acid :—



The author at first thought that the decomposition of the cyanides of the heavy metals into hydrocyanic acid and chlorides by muriatic acid might be employed for the determination of the cyanogen in these compounds. But when the compound to be analysed, as for instance cyanide of mercury or zinc, was mixed with muriatic acid in a small retort and distilled directly into ammonia, the results were very erroneous. He obtained, instead of 0.750 grm. of cyanide of mercury, 0.717 grm.; instead of 1 grm., 0.874 grm.; and instead of 0.49 grm. of cyanide of zinc, 0.451 grm. These great differences are probably caused by the decomposing action of the muriatic acid upon the hydrocyanic acid, with formation of formiate of ammonia.

The copper method is particularly advisable in the determination of the amount of hydrocyanic acid in officinal bitter-almond water, as the silver method gives no such distinct indications, in consequence of the turbidity of the fluid. When ammonia is added to bitter-almond water, the fluid at first undergoes no change, but in a few minutes becomes turbid, and after a time quite opake. The body separated is hydrobenzamide, and its formation is explained by the following formula :—



Hydride of benzoyle.

Hydrobenzamide.

When heated in a glass tube, ammonia is evolved, and renders reddened litmus-paper blue. When boiled with caustic potash, ammonia is also abundantly evolved, and the fluid remaining, when saturated with muriatic acid and left to cool, deposits lance-shaped crystals of benzoic acid. The turbidity has no injurious influence upon the copper test, and the blue colour may be as distinctly recognized as in a clear solution.

20 cub. centims. of bitter-almond water required 4.5 cub. centims. of normal silver solution to form a constant precipitate.

40 cub. centims. took 8.95 cub. centims.	} of normal copper solution.
20 4.5 ...	
20 4.5 ...	

According to both methods the bitter-almond water contained 0.1215 per cent. of anhydrous hydrocyanic acid.

To avoid the injurious effect which may be produced by sucking even very dilute hydrocyanic acid into the pipette, especially when often repeated, the author has given a new arrangement for that piece of apparatus. A thin tube of vulcanized india-rubber is attached to the sucking end of the pipette, and furnished at the other end with a chloride of calcium tube, filled with caustic lime and sulphate of soda, and provided with a glass point for sucking. A stop-cock is introduced between the chloride of calcium tube and the pipette. When the cock is open the fluid is sucked up beyond the mark, to which it is allowed to sink exactly by careful pressure of the stop-cock. In this manner even very strong hydrocyanic acid may be measured.—Liebig's *Annalen*, May 1855, vol. xciv. p. 198.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Behaviour of some Bodies at elevated Temperatures, and particularly of several Colouring Matters under the Glazing of Pottery. By J. G. GENTILE.

THE author has studied the behaviour of some bodies when exposed to a long-continued high temperature. He employed a pottery-furnace arranged in the English manner, which was gradually more and more strongly heated, and which continued heated for forty-two hours. The material to be tested was contained in red unglazed crucibles; these were placed in a baked fire-clay vessel, which was put into the hottest part of the furnace. Common salt was frequently added to the mixed materials, either as a flux or as a covering.

These experiments fall into three divisions, showing,—I. the behaviour of certain materials and mixtures when heated; II. how some of them behaved under glazing; these were laid on a piece of red ware with a brush, covered as usual with lead glazing containing borax, and exposed to the heat of the glazing-furnace; and III. the action of some metallic chlorides in the common pottery-furnace and under glazing upon different substances.

I. *Substances and Mixtures, exposed to the Heat of the common Pottery-furnace.*

1. *Potash-felspar*, from Ytterby, powdered, furnished a coherent semitransparent mass, which was distinctly vitrified, without however having been completely fluid.

2. *Cornish-stone*, from England, ground, behaved in exactly the same manner, except that the colour was yellower. It is a half-decayed stone, which contains felspar and quartz, and furnishes kaolin by washing.

3. *Bichromate of potash* leaves oxide of chrome in small crystalline laminae, attached to the margins of the vessel. When they are furthest apart, they exhibit different colours according to the direction in which the light falls upon them.

4. *Ground window-glass* was converted into a streaky, dull and glassy mass, which had evidently been quite fluid.

5. *Sulphate of zinc* lost every trace of sulphuric acid. The oxide of zinc remained in the form of a yellowish powder, which dissolved very readily in acids.

6. *Sulphate of Copper*.—The residue of oxide of copper becomes so fluid, that it eats through the crucible, flows out, and even runs through some saggars. It crystallizes in a radiating form, but is much contaminated with silica.

7. Metallic copper and silver both fuse. The former becomes so fluid that it runs out of the crucible into the sagger; it acquires a thin coating of red protoxide of copper.

8. *Oxide of Chrome and Oxide of Iron*.—3 parts of oxide of iron, employed as English red, and 1 part of bichromate of potash (6 equivs. of the potash-salt to 1 equiv. of oxide), furnish a black crystalline mass, which contains a little neutral chromate of potash. When washed, it gives a deep black colour under glazing on pottery.

9. 3 parts of oxide of iron and 2 parts of bichromate of potash also furnish a black mass, but its powder is brownish. Under lead glazing it becomes deep brown.

10. 2 parts of oxide of iron and 1 part of bichromate of potash furnish a mass similar to the preceding. Under glazing it gives a brownish-black colour.

11. Equal parts of oxide of iron and bichromate of potash, with 2 parts of common salt, gave a very black mass, shining with numerous crystalline surfaces. The outside of the crucible was covered with a satin-like coating of green crystals of oxide of chrome.

12. 1 part of chrome-black, prepared according to the process previously described by the author, by the calcination of sulphate of zinc with bichromate of potash, was mixed with 2 parts of common salt, and moistened with a little carbonate of potash. It gave a porous mass, crystallized throughout, and of extraordinary lustre, and the bottom of the crucible was covered externally with crystals of oxide of chrome.

13. The same black, mixed with an equal quantity of carbonate of soda, gives no better result than No. 8; the crystals are small.

14. 1 part of metallic iron, 1 part of bichromate of potash, and 1 part of common salt gave a very hard dense mass, which was scarcely acted upon by muriatic acid, and possessed the lustre and fracture of chrome-iron ore. It had the form of the iron employed, and consequently was not fused.

15. 1 part of oxide of iron, 2 parts of bichromate of potash, and

2 parts of common salt furnished a black mass lying at the bottom, above which there were very thin crystals of oxide of chrome containing iron, of a brown colour by reflected, but a beautiful ruby-red by transmitted light.

16. 2 parts of oxide of chrome, 1 part of oxide of iron, and 1 part of iron turnings, covered with common salt, gave a fused and entirely crystalline mass, in which distinct octohedra were recognizable.

17. The oxide of iron that occurs in commerce (English red), exposed to heat by itself, does not fuse, but becomes vitrified, forming a very hard mass, which does not amount to more than a quarter of the original volume; it is broken with difficulty with an iron hammer.

18. *Oxide of Chrome and Oxide of Zinc.*—2 parts of bichromate of potash and 6 parts of metallic zinc furnished oxide of chrome and oxide of zinc separately. 1 part of the zinc remained in the metallic state.

19. 1 part of crystallized sulphate of zinc and 1 part of bichromate of potash (about equal equivalents) furnished a black, perfectly crystalline mass, in which octohedra were recognizable. The crystals have a strong lustre, and when pounded give a black powder; under glazing they produce the same colour as the author's chrome-black. The mass is scarcely acted upon by acids; nitrate of potash, fused with it, dissolves the oxide of zinc with evolution of gas, before attacking the oxide of chrome, which long resists its action, retaining its green colour.

20. 4 parts of oxide of zinc and 4 parts of bichromate of potash furnished a yellowish mass, which became brown by washing. When employed under glazing, it gave an impure dingy brown colour, which penetrated into the mass of the earthenware.

21. 2 parts of oxide of zinc, 4 parts of bichromate of potash, and 2 parts of common salt furnish, without fusion, a lilac-coloured mass, which still contains chromate of potash. When repeatedly heated to redness with 2 parts of common salt and 1 part of carbonate of soda, it undergoes no change.

22. 2 parts of oxide of zinc, 2 parts of oxide of chrome, and 4 parts of common salt gave a brownish mass, which underwent no change by repeated calcination.

23. *Oxide of Iron and Oxide of Zinc.*—4 parts of sulphate of zinc and 8 parts of crystallized sulphate of iron furnished a fused mass, which was partly of a silvery white colour, and shining like porphyry. At the edges of the crucible it was crystalline, and had the appearance of zincblende; in some places it was red and translucent; its powder was brown.

24. 2 parts of oxide of iron and 2 parts of sulphate of zinc furnished a mass, blackish-gray above, brown beneath; the upper portion exhibited traces of crystallization. Its fracture also was brown.

25. 2 parts of protoxide of iron, 2 parts of sulphate of zinc, 2 parts of common salt, and 1 part of nitrate of potash gave a fused reddish-brown mass, the cavities of which were filled with shining crystals.

26. *Borate of Zinc.*—Equal parts of borax and sulphate of zinc

ate through the crucible. A beautiful, shining, colourless glass ran out, and a piece of perfectly clear sulphate of soda, which looked like glass, but showed some clefts, was left in the crucible.

27. *Oxide of Chrome and Oxide of Copper*.—Chromate of copper (the brown precipitate produced in sulphate of copper by neutral chromate of potash) furnished a black crystalline mass, which gave a brownish-black colour under glazing.

28. 3 parts of copper-turnings and 1 part of bichromate of potash furnished without fusion, a green crystalline mass, of the form of the copper-turnings; they are however swelled up to at least 10 times their volume. Nitric acid dissolves the copper from this with effervescence. Hydrogen gas only reduces the protoxide of copper contained in it.

29. 5 parts of sulphate of copper, $1\frac{1}{2}$ part of bichromate of potash, and 2 parts of common salt gave a fused black mass, which only exhibited crystals in a few spots.

30. *Copper and its oxides*.—4 parts of metallic copper (galvanic), covered with 4 parts of common salt, gave a fused saline mass (from which a yellowish-white chloride of copper could be separated by lixiviation), with scattered needles of peroxide of copper. The remainder of the copper was found united into a regulus at the bottom of the crucible.

31. Copper, put in without covering, fused and acquired a coating of red protoxide of copper.

32. 1 part of copper-filings and 1 part of muriate of ammonia furnished a fused, red, radiating mass of protoxide of copper, beneath which was a metallic regulus, like that furnished by copper alone.

33. *Oxide of Chrome and Oxide of Manganese*.— $3\frac{1}{3}$ parts of pulverized oxide of manganese and 1 part of bichromate of potash furnished a brown porous mass, which still contained a little neutral chromate of potash; this may be extracted by water. When triturated the mass gives a brown colour under glazing.

34. 2 parts of oxide of manganese, 1 part of bichromate of potash, and 1 part of common salt gave a black non-crystalline mass.

35. 1 part of oxide of manganese, 1 part of bichromate of potash, 1 part of silica, and 3 parts of common salt furnished a fused mass, which, when taken out, was still covered with common salt; after this had been washed off, the surface of the mass was seen to be coated with octohedra.

36. 1 part of oxide of manganese, 4 parts of bichromate of potash, 1 part of silica, and 3 parts of common salt gave a porous mass, with a few black octohedra.

37. 1 part of oxide of manganese and 1 part of bichromate of potash, fused under a coating of common salt, furnished a bronzed green mass, which exhibited no trace of crystallization.

38. 2 parts of oxide of manganese, 2 parts of bichromate of potash, and 3 parts of silica, fused under a thin layer of common salt, furnished a brown mass, the cavities of which contained black octohedra.

39. 2 parts of oxide of manganese, 2 parts of bichromate of potash, 2 parts of silica, and 1 part of crystallized carbonate of soda produced a dark reddish-brown opaque mass, without any indications of crystallization. A considerable quantity of crystalline oxide of chrome was deposited on the crucible.

40. 1 part of oxide of manganese and 2 parts of bichromate of potash, covered with common salt, furnished a fine, black, crystalline mass, with distinct octohedra. Under glazing this gave exactly the same reddish violet-brown colour which, under the name of *mulberry colour*, is often used on English crockery.

41. The residue of No. 33, again exposed to heat, gave a porous mass, crystalline throughout; the crystals showed distinct octohedral faces. The mass gave a dark brown under glazing.

42. Equal parts of crystallized protosulphate of manganese and bichromate of potash furnished above a black crystalline mass, which gave a blackish-brown powder and a similar colour under glazing; beneath this was an olive-brown mass, which produced the same colour under glazing. When again heated with common salt, it underwent no change.

43. *Oxide of Manganese and Silica*.—24 parts of oxide of manganese mixed with 2 parts of silica do not fuse, but cake together a little. When this mass is pulverized and mixed with common salt, a compound is obtained which is crystalline throughout; its surface exhibits a few separate octohedra.

44. 4 parts of oxide of manganese, 2 parts of silica, and 1 part of crystallized carbonate of soda furnish a somewhat amorphous, dark reddish-brown glass, without flaws.

45. 7 parts of oxide of manganese and 4 parts of silica behave like No. 43. The mass, fused with common salt, is very crystalline, radiate and gray.

46. 4 parts of oxide of manganese and 5 parts of silica, mixed with common salt, scarcely fuse; however, the fracture of the vitrified mass is crystalline, brownish and gray.

47. *Oxide of Manganese and Oxide of Iron*.—4 parts of oxide of iron, 1 part of oxide of manganese, and 2 parts of silica gave a dark brown, or nearly black, crystalline mass.

48. 5 parts of oxide of manganese, 90 parts of kaolin, 5 parts of borax, and 10 parts of silica do not fuse, unless after the addition of common salt. Brownish-red radiating crystals are formed upon the sides of the crucible, and some bubbles were filled with similar crystals. (The mixture was made for the preparation of artificial tourmaline.)

49. *Oxide of Chrome and Oxide of Lead*.—Chromate of lead, employed as chrome-red, melts into a brown mass, which furnishes a dingy brown powder. On the surface there was a thin stratum of a fiery-red colour, which was crystallized in a radiate form. The crucible was strongly acted upon.

50. Neutral (yellow) chromate of lead, covered with common salt, penetrated completely into the crucible, on which it left some dingy chrome-green.

51. *Tin and Oxide of Tin*.—Granulated tin, when taken out of the crucible, had a coating of white oxide of tin, on the lower surface of which there were perfectly clear needles of oxide of tin with an adamantine lustre. At the bottom there was a beautiful yellow transparent glass, which enclosed metallic tin.

52. *Oxide of Tin and Oxide of Chrome*.—2 parts of oxide of tin, $\frac{1}{8}$ part of bichromate of potash, and 1 part of efflorescent carbonate of soda furnished an amorphous lilac colour, which gave a purple colour under glazing, similar to the purple for stone-ware prepared in England by mixing pink colour with oxide of cobalt.

53. Pink colour, prepared by Malaguti's process, mixed with equal parts of common salt and saltpetre, furnished a far more beautiful rose-red colour, which however still gave the tint of pink colour under glazing.

54. Pink colour, mixed with half its quantity of phosphate of lime and heated to redness, undergoes no change, but gives a beautiful rose colour under glazing, and is not so easily burnt off as pink colour thinly laid on.

55. *Oxides of Cobalt*.—Protochloride of cobalt, exposed to the red heat of a muffle-furnace, is completely converted into Co^3O_4 , and covers the walls of the crucible with regular black octohedra of great lustre. This compound is consequently isomorphous with the similarly-constituted magnetic iron FeO , Fe^2O^3 .

56. *Sulphuret of Cobalt*.—Oxide of cobalt, mixed with sulphur, allows the sulphur to evaporate without any action; but if powdered sulphur be thrown upon oxide of cobalt at a strong red heat, a steel-gray fused mass, the fracture of which has the lustre of cobalt-glance, is formed at the bottom of the crucible, and above this is a pulverulent mass, which has nearly the lustre and colour of brass.

57. *Metallic Cobalt*.—Oxide of cobalt, mixed into a paste with linseed-oil and rye-flour, and covered with powdered glass, gives a spongy metal, which is only fused close to the crucible. The fresh fracture of this portion looks like white iron.

58. *Oxide of Chrome and Oxide of Cobalt*.—Protochromate of cobalt fuses to a bluish-green mass, with small black octohedra in some places.

59. *Magnesia and Oxide of Iron*.—Crystals of impure Epsom salts (containing 2 equivs. of sulphate of magnesia to 1 equiv. of protosulphate of iron) furnished, without fusion, a clear, yellowish-red, porous mass. Water extracted sulphate of magnesia without any traces of oxide of iron.

60. *Magnesia and Oxide of Chrome*.—2 parts of sulphate of magnesia and 2 parts of oxide of chrome left a swelled dingy oxide of chrome. The edge of the crucible was coated with small black crystals.

61. 2 parts of magnesia alba, 2 parts of bichromate of potash, and 2 parts of common salt were exposed to heat at the same time with No. 21. The yellowish-greenish-gray mass obtained gave, under glazing, a dingy brownish-green, which penetrated the biscuit. The

mass, when again heated to redness, becomes reddish-brown, and grows darker when repeatedly mixed with common salt and calcined; some parts of it are black and crystalline.

62. *Oxide of Bismuth and Oxide of Chrome*.—2 parts of oxide of chrome, 2 parts of basic nitrate of bismuth, and 2 parts of common salt gave a mass which was partly green, partly yellow. The two oxides remained distinctly separated.

II. *Substances exposed to the Heat of the Glazing-furnace, laid upon Biscuit-earthenware, under a Glaze containing Lead and Borax.*

1. Chromate of lime gives a yellowish-green colour. Distinct crystals of oxide of chrome are recognizable under the glazing.

2. Basic chromate of copper, the reddish-brown precipitate referred to under No. 27, laid on without calcination, gives a dark brownish-red colour, in which brown crystalline spangles are observable.

3. Chromate of iron and basic chromate of iron (the precipitate formed by bichromate of potash with chloride of iron) give a dingy green, with a tendency to brown.

4. Chromate of cobalt gives a very blue green, of no beauty.

5. Chromate of lead behaves nearly like chromate of lime. The colour is less yellow, but more dingy.

6. Protochromate of iron (the precipitate produced in sulphate of iron by neutral chromate of potash), when laid on without calcination, gives a strong black colour, like that of the author's chrome-black.

III. *Influence of common Salt, and some other Chlorides, upon Colouring Matters in a free state and under Glazing.*

1. If the earth of the sagger which is employed in the burning of earthenware contains common salt, oxide of iron is volatilized from the materials, and deposits itself upon the angles of the pieces, which it colours red and glazes a little; it also causes a difficulty in the glazing, as the glaze does not readily adhere to these places.

2. If a piece of earthenware which has been burnt red be furnished with a glazing, which, although otherwise of good quality, has been mixed with only 2 to 3 per cent. of common salt, not only is this piece deprived of its glazing, but the whole of the earthenware in the saggars, both above and below it, will lose theirs, even though the saggars only communicate with each other by cracks in their bottoms. The cause is probably the volatilization of the lead in the form of chloride. Nitrate or carbonate of soda, employed instead of the salt, only cause the glazing to flow more readily.

3. If a larger quantity of common salt be placed dry in a sagger containing glazed earthenware, printed with colours which are to make their appearance after the fusion of the glazing, the latter is not injured, but the following effects are produced upon the colours:—

a. All oxide of cobalt colours are partially volatilized, so that the blue is diffused like a cloud over the whole piece, especially in the neighbourhood of the printed parts. The white has there a very agreeable bluish tint, and the blue appears somewhat washed out; this is the mode of production of the English *flowing-blue*. Black, containing oxide of cobalt, and English purple, consisting of pink colour mixed with oxide of cobalt, also give blue clouds. To prevent the too great volatilization of the cobalt, an addition of minium ($\frac{1}{32}$) may be made to the colour, or some nitrate of potash may be mixed with the salt.

b. Oxide of copper colours also diffuse themselves at a strong heat with a greenish tinge. If a capsule be soaked in a solution of sulphate of copper, and employed in glazing earthenware in the presence of salt, all the earthenware acquires a greenish colour.

c. Common salt has no action upon pink colour, or colours derived from antimony and oxide of chrome, at least at the usual temperature.

d. It acts upon oxide of nickel colours in the same way as upon oxide of cobalt. They become diffused in the same manner, giving the earthenware a grayish-violet colour, which is often seen on English earthenware upon which black colour containing nickel has been used. It behaves in the same way with blue containing nickel, producing what is called *Indian blue*.

e. If the author's chrome-black be exposed to the vapours of a mixture of common salt and saltpetre, it becomes greenish, and surrounded with a yellow margin.

4. Chlorides of calcium and lead act upon colours in the same way as common salt, and muriate of ammonia has the same influence upon oxide of cobalt. Oxide of cobalt is converted into chloride by muriate of ammonia, even at a very gentle heat; ammonia is evolved.

The actions of these chlorides are employed in England in the production of the so-called *flowing-colours*, either by covering the saggars with a mixture of chloride of calcium or lead and China clay, or by placing these materials in small crucibles beside the earthenware. They succeed better in proportion as the glazing itself contains less lead, and at particular temperatures. In all cases the saggars must be perfectly closed, as otherwise the colours are too much volatilized; or, if smoke can get in, a variety of other colours are produced by reductions, the chemical nature of which is not yet ascertained, and which cannot be obtained by design. Black, rough, and bladdery spots are also produced by the reduction of lead, and the lead glazing is particularly sensitive to smoke in the presence of these chlorides.

5. The metallic chlorides only appear to act upon oxide of manganese at a far higher temperature. Sometimes spots coloured by oxide of manganese are seen on ware which has been placed in the middle of the furnace; this oxide of manganese appears to have been volatilized in a similar manner, from the combustible materials employed.—*Polytechn. Journal*, cxxxv, p. 205; *Centralbl.* 1855, p. 559.

Black Stain for Wood. By C. KARMARSCH.

The author having learnt from Professor Altmüller, of Vienna, that Runge's black stain, which has been much recommended for some years as an ink for steel pens, furnished an excellent means of staining wood black, was induced to make some experiments, the results of which lead him to recommend it further for this purpose.

The ink in question, which may be readily prepared by any one, is applied to the wood without warming, or any other preparation, by means of a brush or sponge. When dry, the application of the dye is repeated, and three, or at the utmost four applications, produce a deep black colour, which acquires the highest beauty when polished or varnished.

The stain may be kept for a long time; and in simplicity of employment, as well as in the goodness and rapidity of its results, it exceeds the common black wood-stain, which it certainly equals in cheapness. The author has obtained equally good results with the most different woods, such as beech, cherry, poplar, lime, fir, &c.

The best method for the preparation of the chrome-ink, according to several comparative experiments, is the following:—4 lbs. or 2 quarts of boiling water are poured over 1 oz. of pounded commercial extract of logwood, and when the solution is effected, 1 drachm of yellow chromate of potash is added, and the whole well stirred. The fluid is then ready for use as a writing ink or wood-stain. It has a beautiful violet-blue colour, as may be seen from the thin stratum which runs down the glass when the bottle is shaken, but when rubbed upon wood it produces a pure black. It may be prepared, even on a small scale, at the price of threepence per quart.

When the extract of logwood cannot be obtained, the preparation is rather more tedious. In this case 4 lbs. of logwood may be extracted by boiling with water for about an hour, and the fluid, separated by decantation and pressing the woody residue, evaporated to about 3 quarts; 1 drachm of chromate of potash is then dissolved in it. The author has obtained remarkably good results in staining wood with a fluid prepared in this manner; but when it stands for a time, it deposits a considerable quantity of black sediment, which shows that it might have more water. Indeed Runge recommends a larger quantity both of water and chromate of potash for the preparation of his chromic ink. According to his receipt, 1000 parts of decoction are to be prepared from 125 parts of logwood, and to this 1 part of chromate of potash is to be added. Perhaps a proportion lying midway between this and the preceding recipe might be the most advisable for a wood-stain, namely, 4 lbs. of logwood to yield 9 quarts of decoction, to which half an ounce of chromate of potash may be added.

The commercial extract is however to be preferred, as with it the preparation is made very quickly and with little trouble.—*Mittheil. des Gewerbevereins für Hannover*, 1854, p. 298.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Decomposition of the Alkaline Silicates by Carbonic Acid, and on the Solubility of Silica in pure Water, as also in the presence of Carbonic Acid, Ammonia, Muriate of Ammonia, and the Bicarbonates. By C. STRUCKMANN.

THE inducement to the following investigations was furnished by the desire, on the one hand, to acquire a clear insight into the decomposition of the rocks containing felspar, so as to obtain some data for the knowledge of soils, and, on the other, to ascertain in what form plants, and especially the graminaceous plants, which are rich in silica, take up that substance from the soil. In the course of the investigations, it was found that they did not always agree with previous observations; and this was especially the case in regard to the decomposition of the alkaline silicates under the influence of carbonic acid, and the solubility of silica in different fluids. Particular attention was therefore paid to these points.

An alkaline silicate, readily soluble in water, was prepared by fusing quartz-sand with carbonate of potash and soda. The aqueous solution contained, in addition to the silicate, a considerable excess of the alkaline carbonates; for on the addition of muriatic acid, a violent and long-continued effervescence took place before the silica began to separate in a gelatinous form.

Considering the various results obtained hitherto in investigations of the behaviour of the alkaline silicates towards water and carbonic acid, it appeared not unimportant to repeat these experiments. Carbonic acid was therefore passed for several days through a dilute solution of silicate of potash and soda. It was not until the carbonic acid had been passing for a long time that a turbidity appeared throughout the whole fluid; but this then rapidly increased, and the whole vessel was soon filled with gelatinous silica. As soon as no further separation appeared to take place, the gelatinous silica was collected upon a filter, and carbonic acid again passed for eight days through the clear filtrate, which had an alkaline reaction, but only a very few flakes of silica separated; these were also filtered, when the filtrate had a slight alkaline reaction, and the addition of muriatic acid produced violent effervescence, without however causing a turbidity or separation of silica in the acid fluid. To ascertain whether

any silica was present in the fluid, 150 grms. of it were evaporated with muriatic acid, and the residue was heated; after the alkaline chlorides were extracted with water, there remained 0.045 grm. of silica completely insoluble in water and acids. 100 grms. of the fluid consequently contained 0.0306 grm., or about $\frac{1}{32}$ per cent. of silica.

Thus, after all the carbonates are converted into bicarbonates, *the alkaline silicate is completely decomposed by the carbonic acid, and the silica is separated in a gelatinous form.* The small quantity of silica which was obtained by evaporating the fluid containing the bicarbonates, was very probably present in the fluid as free silica. The results obtained by G. Bischof, however, are completely opposed to these. He passed carbonic acid through an alkaline silicate, but observed no separation of silica; he infers, as the solution then contained alkaline carbonates, that a decomposition of the silicate had certainly taken place, but in such a manner that an acid silicate had been formed simultaneously with the alkaline carbonate (Bischof, *Lehrb. der Geologie*, i. 2, p. 824). In another place he says expressly, that alkaline silicates, even in concentrated aqueous solutions, remain undecomposed in the presence of a great excess of carbonic acid (p. 511). It is however to be supposed that Bischof did not continue the passage of the carbonic acid long enough. And even if he made use of a very dilute solution of the silicate, from which no considerable separation of silica could be produced, the supposition that an acid silicate is formed is not admissible, for we have already seen that after the filtration of the silica separated by carbonic acid, muriatic acid effects no further separation in the filtrate, which however must have been the case if an acid silicate had been present, as this would certainly be decomposed by the muriatic acid.

Moreover, other chemists have already shown that an alkaline silicate is completely decomposed by carbonic acid; Doveri has proved this, and Liebig expressly says *that the soluble silicates are completely decomposed by carbonic acid*; that a solution of soluble glass sets into a jelly when carbonic acid is passed through it; that this decomposition takes place even in very dilute solutions, and in this case the silica probably remains dissolved in the water (Liebig, *Agriculturchemie*, ed. 6, p. 112).

From what has been stated, these experiments of Bischof's cannot be regarded as trustworthy, and the geological conclusions which he derives from his investigations upon this subject are also rendered untenable, namely, "that alkaline silicates may be present in waters under all circumstances in company with alkaline carbonates or bicarbonates, and that it is consequently quite indifferent whether the waters only contain a small quantity of carbonic acid, or whether they are saturated with carbonic acid."

From the results of the preceding experiments we may rather come to the conclusion, that when waters are fully saturated with carbonic acid, a complete decomposition of the alkaline silicates contained in them will take place, and that consequently waters con-

taining carbonic acid flowing from felspathic rocks, contain, besides carbonates and bicarbonates, free silica in solution, whilst waters free from carbonic acid will rather contain alkaline silicates together with the carbonates.

In order to determine the solubility of silica in different solvents, the silica precipitated in a gelatinous form from silicate of soda and potash was first washed with water, then treated for a considerable time with cold muriatic acid, and again washed with cold water until the washing-water no longer showed any turbidity with protonitrate of mercury. The pure silica was then left in contact with the fluids in question for a long time with frequent stirring, the portion remaining undissolved was separated by filtration, and a certain weight of the filtrate evaporated to dryness; the residue, which consisted of fine white laminae, was always pure silica.

From these experiments the following results were obtained:—

1. 100 parts of pure water, digested with hydrated silica in the cold, dissolve 0.021 part, or about $\frac{1}{48}$ per cent. SiO_3 .

2. 100 parts of pure water, through which carbonic acid was passed interruptedly for thirteen hours and a half in the course of six days, whilst it was in contact with hydrated silica in a glass cylinder, dissolved 0.0136 part of silica, or about $\frac{1}{74}$ per cent. Hence the comparative solubility of silica in pure water and water impregnated with carbonic acid is seen to be as 3 to 2.

3. 100 parts of dilute muriatic acid of spec. grav. 1.088, digested for eleven days in the cold with hydrated silica, dissolved 0.0172 part, or about $\frac{1}{59}$ per cent. of silica. When the solution in muriatic acid was slowly evaporated, tufts of acicular crystals of hydrated silica were deposited upon the sides of the porcelain dish, as already observed by Doveri. The comparative solubility of silica in pure water and dilute muriatic acid is as 5 to 4.

4. 100 parts of a solution of carbonate of ammonia, containing 5 parts of dry sesquicarbonate of ammonia and 95 parts of water, dissolved 0.02 part, or $\frac{1}{50}$ per cent. of silica.

5. 100 parts of a very dilute solution of carbonate of ammonia, containing only 0.1 per cent. of dry sesquicarbonate of ammonia, dissolved 0.062 part, or about $\frac{1}{16}$ per cent. of silica. There is consequently a very considerable difference between the solubility of silica in the more concentrated and in the very dilute solutions of carbonate of ammonia. In the one case the carbonate of ammonia appears to have exercised no influence at all upon the solubility of the silica, for pure water dissolves about the same quantity. On the other hand, in a very dilute state the carbonate of ammonia decidedly increased the solubility; it is to be supposed that a part of the silica combined with a portion of the carbonate of ammonia to form silicate of ammonia, but that during the evaporation of the solution the salt was decomposed, leaving pure silica; and this is rendered still more probable by the following experiments:—

When a portion of this last solution of silica was left standing in the air in a vessel that was not closely stopped, a turbidity was soon observed in the fluid, and small flakes of silica separated; the silicate

of ammonia was probably again decomposed by the formation of bicarbonate of ammonia. The flakes were separated by filtration, and when a certain quantity of the filtrate was evaporated, it was found that 100 parts still retained in solution 0.0288 part, or about $\frac{1}{34}$ per cent. of silica. We have already seen that a nearly equal quantity of silica (0.0306 in 100) was retained in solution by the fluid containing bicarbonate of soda and potash, which is at any rate an interesting concordance.

6. 100 parts of an ammoniacal fluid, containing 19.2 per cent. of anhydrous NH_3 , digested in a closed vessel with hydrated silica, dissolved 0.071 part, or about $\frac{1}{14}$ per cent. of silica.

7. 100 parts of a diluted ammoniacal fluid, containing 1.6 per cent. of anhydrous NH_3 , dissolved under the same circumstances 0.0986 part, or nearly $\frac{1}{10}$ per cent. of silica.

Solutions of ammonia, especially when diluted, consequently increase the solubility of silica very considerably, and it can hardly be doubted that this is caused by the formation of silicate of ammonia. I shall again refer to this point.

The results of the foregoing experiments do not agree in part with the observations of I. Fuchs, who states that 100 parts of cold water dissolve only 0.013, and 100 parts of dilute muriatic acid of spec. grav. 1.115 only 0.009 of silica*. This difference may perhaps be explained in the following manner, that Fuchs made his experiments with silica prepared by passing gaseous fluoride of silicium into water, and that this silica perhaps possesses a lower degree of solubility than that prepared by passing carbonic acid into an alkaline silicate. The relative proportion of the solubility of silica in pure water and dilute muriatic acid is nearly the same in the experiments of Fuchs and myself (as 3 to 2 according to Fuchs, as 6 to 5 in my experiments), and the agreement would perhaps be still closer if the muriatic acid employed had possessed the same specific gravity.

The results of these experiments upon the solubility of silica lead to the following conclusions:—

1. All waters may contain free silica in solution.
2. Waters free from carbonic acid will either contain the silica in the form of silicates, or as free silica, according to the nature of the rocks through which they flow; the first form will probably be the most general.
3. Waters impregnated with carbonic acid may also contain free dissolved silica.
4. In the gradual decomposition of the alkaline silicates in the soil, in which carbonic acid will always take a considerable part, the silica will always be separated as free silica if a sufficient excess of free carbonic acid be present; this silica, however, as its quantity can never be very considerable at one time, will for the most part be dissolved in water. It is therefore probable that in most cases plants will take up the silica necessary for their nourishment in the form of dissolved free silica. This view also finds support in the

* Liebig's *Annalen*, lxxxii. p. 119.

large amount of silica, with a proportionably small quantity of alkalis, in the ashes of cereals and grasses, as may be seen particularly from Haidlen's analysis of the ashes of good meadow hay*. He found in 100 parts of ashes,—

Silica	60·1
Phosphate of lime	16·1
Phosphate of iron	5·0
Lime	2·7
Magnesia	8·6
Sulphate of lime	1·2
Sulphate of potash	2·2
Chloride of potassium	1·3
Carbonate of soda	2·0
Loss	0·8

This great excess of silica could not be combined with alkali; it must consequently be admitted that a considerable portion of it must have been taken up by the plant in the form of free dissolved silica.

5. The circumstance that ammonia and carbonate of ammonia may favour the solubility of silica in water, renders it probable that silica may dissolve in water containing ammonia in the form of silicate of ammonia. But in order to obtain more decided results upon this last point, the following experiments were made:—

I. An aqueous solution of a silicate of potash and soda was mixed with carbonate of ammonia, and the silica separated washed upon a filter with distilled water until the washing-water no longer exhibited any turbidity with chloride of mercury; no carbonate of ammonia could therefore be mixed with the silica, and any ammonia present must be chemically combined with the silica. After this had been dried a little upon the filter, but had not lost its gelatinous consistence, a portion of it was put into a porcelain cup, and pure solution of soda was poured over it. A small rod with muriatic acid was then held over it, *when distinct vapours of muriate of ammonia arose*, so that ammonia was combined with the silica.

Nine days later, when the silica had dried in the air and acquired an earthy consistency, another portion was tested for ammonia in the same manner, and the evolution of vapours of muriate of ammonia, although in small quantity, was again observed; the silicate of ammonia was consequently not completely decomposed. This supposition received a stronger confirmation by the quantitative determination of the amount of ammonia contained in a portion of the air-dried silica, a weighed quantity being mixed with a few drops of muriatic acid, evaporated and moderately heated; the muriate of ammonia formed was separated by water from the insoluble silica, and the aqueous solution evaporated with chloride of platinum, when it was calculated from the quantity of ammoniochloride of platinum, that 2·6 milligrams. of ammonia were combined with 230·7

* Liebig's *Agriculturchemie*, ed. 6, p. 293.

milligrams. of the silica in question; and if we adopt the formula NH^4O , SiO^3 for silicate of ammonia, 2.6 of ammonia will represent 7.1 of neutral silicate of ammonia. 100 parts of the silica examined therefore contained 3.1 parts of silicate of ammonia, which is certainly a very small quantity; but this proves that a portion of the silicate of ammonia may exist even in the air-dried state.

II. Another portion of the aqueous solution of silicate of soda and potash was mixed with muriate of ammonia, and the separated gelatinous silica washed on a filter with distilled water until the washing-water no longer produced any turbidity with protonitrate of mercury. When the silica was a little dried, it was tested as above for ammonia, and an abundant formation of fumes was observed, so that silicate of ammonia is formed in this case also. Nine days afterwards, only a slight formation of vapours could be seen with another portion. Four weeks later, the amount of ammonia in a weighed portion of the silica was again determined, as in the preceding experiment. 100 parts however only contained 1.46 of silicate of ammonia (NH^4O , SiO^3), or half as much as the preceding portion.

The results of these investigations therefore allow us to draw the following conclusions with regard to the formation of silicate of ammonia:—

1. It must be admitted that silica in the gelatinous state is capable of combining chemically with ammonia.

2. When silica loses its gelatinous state by drying in the air, it also gradually loses its power of holding ammonia in chemical combination; the decomposition takes place slowly, for silica which had been exposed to the air for several weeks still contained a small portion of silicate of ammonia.—Liebig's *Annalen*, June 1855, vol. xciv. p. 337.

On Stibæthylum and its Compounds. By R. Löwig.

In an inaugural dissertation, the author gives the results of an investigation, which is a continuation of the well-known one by his father.

Iodide of Stibæthylum, $\text{StAe}^4\text{I} + 3\text{HO}$.—This body is formed when stibæthyle and iodide of æthyle are allowed to act upon each other. The two fluids mix together, but only act upon each other slowly. When enclosed by fusion in a glass tube and heated to 212°F ., the combination takes place very rapidly, and much heat is suddenly set free. The best mode of obtaining it is by mixing equal parts of stibæthyle and iodide of æthyle, putting the mixture into a retort filled with carbonic acid, nearly filling this with water, and closing it by fusion. This is then laid in boiling water, when the combination takes place in two or three hours. The solution is allowed to cool and evaporate on the water-bath, during which process it acquires a somewhat yellow colour, which however may be got rid of by the addition of a few drops of ammonia.

Properties.—Iodide of stibæthylum crystallizes in beautiful hex-

agonal prisms, often an inch in length, or in small pointed crystals, which acquire a yellowish colour in the air. It has a very bitter taste. 19.02 parts of it dissolve in 100 parts of water at 68° F.; it dissolves more easily in absolute alcohol, but in æther with more difficulty than in water. The analyses (a) are of the hydrated and (b) of the anhydrous salts:—

	(a.)	(a.)			(b.)	(b.)		
Sb	..	..	1 = 129	32.33	..	.. = 1	34.33	
C	24.25	24.03	16	96	25.75	25.84	16	25.80
H	6.28	5.95	23	23	5.64	5.58	20	5.47
I	32.24	31.88	1	127	31.83	34.38	34.17	1
O	..	..	3	24	6.01			

During the crystallization of iodide of stibæthylum, especially when it separates from warm solutions, another salt is often formed, with a different amount of water, $2(\text{StAe}^4 \text{I}) + 3\text{HO}$.

Iodide of Stibæthylum and Mercury, $3\text{HgI} + (\text{StAe}^4 \text{I})$.—When a solution of perchloride of mercury is added to a solution of iodide of stibæthylum, a white precipitate is produced, which melts into an oily fluid even at a gentle heat.

This salt is insoluble in water and æther, and dissolves with difficulty in boiling alcohol. It crystallizes from this solution in columnar crystals. If the precipitate be allowed to melt under water of 158° F., it solidifies to a white mass, and only exhibits single red spots, but becomes entirely red after some time. If the mass which has become red be dissolved in boiling alcohol, the white salt separates again in hexagonal prisms. Both forms of the salt have the same composition, but the red crystals appear to belong to the regular system. This salt gave on analysis,—

Stibæthylum.....	..	..	1 = 245	23.27
Mercury.....	29.30	28.40	3	300
Iodine.....	49.00	48.60	4	508

A similar compound, $3\text{HgI} + 2(\text{StAe}^4 \text{I})$, is obtained by adding iodide of mercury to a hot solution of iodide of stibæthylum, until it no longer loses its red colour. The conversion of the excess of iodide of mercury is then effected by a fresh addition of iodide of stibæthylum. None of the latter remains in the fluid; the precipitate melts when heated, forming a yellow oil. Analysis:—

Stibæthylum.....	..	..	2 = 490	34.38
Mercury	20.86	21.80	3	300
Iodine	44.56	44.52	5	635

Chloride of Stibæthylum, $(\text{StAe}^4 \text{Cl}) + 3\text{HO}$, is obtained by saturating oxide of stibæthylum with muriatic acid, or by decomposing 4 atoms of iodide of stibæthylum with 3 atoms of perchloride of mercury, by which means 3 atoms of chloride of stibæthylum are obtained. In the latter case the solution contains neither iodine nor mercury. The salt crystallizes, and deliquesces more readily even than chloride of calcium. It loses its water of crystallization on the

water-bath. It has a strongly bitter taste. The analysis of the dry salt gave,—

Sb		..	..	1 = 129	56.03
C		33.29	33.21	16 96	34.29
H		7.76	7.63	20 20	7.01
Cl		11.13	12.50	Cl 35	12.67

Chloride of Stibæthylum and Mercury.—Compounds exactly similar to those of iodide of mercury with iodide of stibæthylum, are obtained by bringing in contact chloride of mercury and iodide or chloride of stibæthylum. 1 atom of iodide of stibæthylum with 3 atoms of chloride of mercury furnish the iodine compound which melts under water, whilst the water takes up the corresponding chloride, $3\text{HgCl} + (\text{StAe}^4)\text{Cl}$. If concentrated solutions of chloride of stibæthylum and perchloride of mercury be mixed, a compound of the formula $3\text{HgCl} + 2(\text{StAc}^4)\text{Cl}$ is obtained. The former salt is soluble in alcohol and water; the latter forms a white powder, which is difficult of solution in water.

Chloride of Stibæthylum and Platinum, $3\text{PtCl}^2 + 2\text{StAe}^4\text{Cl}$.—This salt is produced by mixing a somewhat dilute alcoholic solution of chloride of stibæthylum with a similar solution of chloride of platinum, and evaporating the mixture. It is a fine yellow compound, tolerably soluble in water and alcohol, which furnished 68.6, 67.2, and 69.2 per cent. of platinochloride of platinum. (Calculation, 68.53 per cent.)

Bromide of Stibæthylum, $(\text{StAe}^4)\text{Br}$, was obtained by saturating oxide of stibæthylammonium with hydrobromic acid. It crystallizes in dazzling white acicular crystals, which dissolve very readily in water and alcohol, and do not deliquesce in the air. Analyses gave 24.39 and 24.37 of bromine. Bromine appears to form bromide of stibæthylum and bromate of stibæthylum with oxide of stibæthylum.

Hydrated Oxide of Stibæthylum, StAe^4O , HO , is obtained by decomposing iodide of stibæthylum with oxide of silver. Traces of dissolved oxide of silver are removed by the careful addition of muriatic acid. The fluid is evaporated *in vacuo*, when the hydrate is obtained in the form of a thick, colourless, oily fluid, of a strongly alkaline and intensely bitter taste, which quickly renders litmus-paper blue. It dissolves in water and alcohol in all proportions, but is insoluble in æther. It sets ammonia free from its compounds, and precipitates the oxides of the heavy metals. Oxide of tin and alumina are again dissolved by the excess of the alkali. The salts of the alkaline earths are not decomposed by the base.

The salts are produced by bringing the base in contact with the acids, or by double decomposition. They have a strong bitter taste.

The sulphate, $(\text{StAe}^4)\text{O}$, SO^3 , crystallizes.

The nitrate, $(\text{StAe}^4)\text{O}$, NO^3 , crystallizes.

The carbonate, $(\text{StAe}^4)\text{O}$, CO^2 , is a tough deliquescent mass.

The formiate, $(\text{StAe}^4)\text{O}$, FoO^3 , forms acicular crystals, difficult of solution.

The acetate, $(\text{StAe}^4)\text{O}$, AcO^3 , forms more soluble acicular crystals.

The succinate, $(\text{StAe}^4)\text{O}$, SuO^6 , does not crystallize.

The oxalate, $(\text{StAe}^4)\text{O}$, C^2O^3 , crystallizes.

The tartrate, $(\text{StAe}^4)\text{O}$, $\text{C}^4\text{H}^2\text{O}^5$, forms large deliquescent crystals.

The bitartrate, $(\text{StAe}^4)\text{O}$, $2(\text{C}^4\text{H}^2\text{O}^5)$, forms fine needles.

The racemate, $(\text{StAe}^4)\text{O}$, $\text{C}^4\text{H}^2\text{O}^5$, forms large deliquescent crystals.

Sulphuret of Stibæthylum, $(\text{StAe}^4)\text{S}$, is obtained by treating oxide of stibæthylum with sulphuretted hydrogen. It is evaporated without access of air, and forms a yellowish oily fluid, which does not crystallize; it dissolves readily in water and alcohol, and behaves like sulphuret of potassium towards the salts of the metals.—*Journ. für Prakt. Chem.*, lxiv. p. 415.

On the Anæsthetic Principle of the Lycoperdon proteus and certain other Fungi. By THORNTON HERAPATH, Esq.

The smoke of the puff-ball, it is well known, has been long employed in some parts of the country, by apiarists, for stupefying bees. In a paper "On the Anæsthetic Properties of the *Lycoperdon proteus*, or common Puff-ball," which was read before the Medical Society of London in 1853, Mr. B. W. Richardson called particular attention to this fact, and stated that the fumes of the burning fungus produced the most perfect anæsthesia, not only in insects, but also in dogs, cats, rabbits, and probably in all the larger animals, and might consequently be applied as a substitute for the vapour of chloroform and æther in producing insensibility to pain in surgical practice. With the assistance of Dr. Willis, he said, he had removed a large tumour from the abdomen of a dog that had been placed under the influence of the narcotic, without any sign of pain being exhibited by the animal during the operation. From this gentleman's experiments it appeared, that when a moderate quantity of the fumes was inhaled slowly, the narcotism came on and passed off slowly, the animal exhibiting all the symptoms of intoxication, with convulsions and sometimes vomiting; but that when they were administered in larger quantity, life was invariably destroyed. The consideration of these and other facts induced Mr. Richardson to conclude, that the peculiar effects that were produced by the inhalation of the smoke of the puff-ball were caused by a volatile narcotic principle contained in the fungus, which was liberated by the action of heat, but was not absorbable by water, alcohol, or a strong alkaline solution. What the exact nature of this principle was, however, he confessed himself to be unable to determine. About eight or nine months ago I carefully repeated Mr. Richardson's experiments, and after making several futile attempts, at last, I believe, succeeded in isolating the narcotic constituent of the smoke.

The first step I considered it necessary to take in the investigation, was to determine in what part of the fungus the anæsthetic ingredient was contained; that is to say, whether in the sporules,

the cellular tissue, or the matters soluble in water. I accordingly digested two or three ounces of the fungus, previously torn up into small pieces, in moderately warm water, and by means of pressure and washing, separated the sporules and soluble constituents from the cellular matter. Then, by allowing the water that had been used in this operation to remain undisturbed for several hours, the sporules were collected in the form of a dark brown-coloured, muddy deposit. This was well washed once or twice with water, and dried in an oven, as was also the cellular matter, and the watery solution was evaporated to dryness. On testing these three substances, it was found that only two of them, namely the sporules and the cellular tissue, were capable of producing anæsthesia; the aqueous extract evolved a thick irritating vapour, but this did not occasion insensibility on inhalation.

It was clear, therefore, that the narcotic principle should be looked for in the two former. Accordingly, small portions of each of them were digested for several hours in boiling alcohol, æther, bisulphide of carbon, wood-spirit, chloroform, diluted sulphuric acid, and fusel oil, but in every instance the residuary matter, when pressed and dried, was found to retain its original narcotic quality. Fresh quantities were then soaked for a considerable period in hot alkaline lye, and in a hot solution of moderately strong nitric acid, until nothing further was dissolved out by either of the reagents; the insoluble portion was well washed with water, and again dried in an oven. On this being tested as before, anæsthesia was found to be no longer produced.

In the next series of experiments I operated in a different way. I introduced the fumes of the burning fungus into bottles containing small quantities of liquor potassæ, dilute hydrochloric acid, alcohol, fusel oil, and diluted sulphuric acid. The bottles were then well shaken for several minutes, and the properties of the purified fumes were tested by introducing flies, bees, or wasps, secured by cement to the ends of long splinters of wood, into the bottles, and observing the effects. In every case, however, insensibility was still produced, thus showing that the narcotic quality of the fumes was not caused by any body soluble in these solutions. There being no substance with which I am acquainted, except carbonic oxide, nitrous oxide, and perhaps some compounds of cyanogen which possess all these properties; and having, moreover, in the mean time read a paper, by M. Adrien Chenol, "*On Pure Oxide of Carbon, considered as a Poison**," it immediately occurred to me that it was the former of these substances that was the cause of the narcotism. I therefore specially examined the fumes for carbonic oxide, by agitating them with an acid solution of chloride of copper, and also by absorbing the carbonic acid, ammonia and oxygen, by means of lime-water, diluted muriatic acid, and a solution of the protosulphate of iron saturated with nitric oxide gas, when indications of the presence of carbonic oxide were readily obtained; the fumes, after agitation with the solution of

* *Comptes Rendus*, No. 16, April 17, 1854.

chloride of copper, no longer induced narcotism ; whilst those, on the contrary, which had been treated with the other solvents, were more than ordinarily powerful, and rendered an insect insensible much more quickly than before ; they also burnt with a blue flame, and possessed all the well-known characters of the oxide of carbon. The correctness of this conclusion was, moreover, confirmed by experimenting with carbonic oxide prepared by acting on oxalic acid with oil of vitriol, and passing the gas evolved through caustic soda-ley. Even when largely diluted with air, it still continued to produce insensibility in insects, and acted in every way like the purified fumes of the *Lycoperdon**.

It is not difficult to understand how carbonic oxide is formed by the ignition of the fungus, as this gas is invariably produced in larger or smaller quantity when certain organic substances are decomposed by heat, though some yield it in greater proportion than others ; and consequently, as might have been anticipated, I find that the fumes of several other fungi act in the same manner towards animals as those of the *Lycoperdon proteus*. The principal of those to which I allude are the common *Lycoperdon* of the druggist, *L. giganteum*, and the mushroom, *Agaricus campestris*. — *Philosophical Magazine* for July 1855.

On the Preparation of the Sulpho-chloride of Mercury in the dry way. By R. SCHNEIDER.

H. Rose has long since shown, that the white precipitate formed during the first period of decomposition by passing sulphuretted hydrogen gas into a solution of perchloride of mercury, is a compound of chloride and sulphuret of mercury in such proportions as to be expressed by the formula $\text{HgCl}_2, 2\text{HgS}$. According to H. Rose, the same compound may be obtained by boiling moist black sulphuret of mercury with an excess of a solution of perchloride of mercury. When prepared by either of these methods, it has the appearance of a white amorphous powder, which is insoluble in boiling water and simple acids, but is readily decomposed by nitromuriatic acid or potash, in the latter case leaving a residue of black oxysulphuret of mercury.

This compound may also be obtained with ease and certainty in the dry way, by enclosing sulphuret of mercury (either black or red) with an excess of perchloride of mercury in closed glass tubes, when, on the application of heat, the sulphuret of mercury dissolves in the fusing chloride, forming a yellowish-brown fluid, which on cooling solidifies into a pearl-gray, enamel-like mass, a mixture of perchloride and sulpho-chloride of mercury. The operation is best performed by means of a Berzelius lamp, at about 662° to 752° F.

* See also 'A Treatise on Poisons,' by Professor Christison, 4th edition, p. 827, for an account of the peculiar effects produced by the inhalation of the oxide of carbon.

and if the tubes are formed of strong hard glass and well closed at the ends, it generally goes on without any disturbance. The perchloride of mercury must be employed in considerable excess if the sulphuret is to be completely dissolved; the quantity should be about 8 to 10 parts of the chloride to 1 of sulphuret (cinnabar); if less of the former be employed, the cinnabar is certainly converted into sulpho-chloride, but a portion of this remains undissolved as a white powder. The excess of perchloride of mercury may be completely extracted from the solid mass by treatment with boiling water; the sulpho-chloride then remains in the form of a dingy white, distinctly crystalline powder. Its analysis gave,—

	Found.	Calculated.
Hg	81.26	81.52
S	..	8.57
Cl	9.68	9.91

In its properties and chemical behaviour, the compound prepared in the dry way nearly agrees with that obtained in the humid way. It is however essentially distinguished from it by its crystalline form, and also by the circumstance that when agitated in water it rapidly sinks to the bottom, and may be very easily washed upon the filter, whilst that prepared in the humid way remains long suspended in the fluid, and causes difficulties in filtration from its producing turbidity in the filtrate.—Poggendorff's *Annalen*, May 1855, vol. xciv. p. 167.

On the Preparation of Schweinfurt Green with Butyric Acid.

By Prof. WÖHLER.

When butyric acid is neutralized with freshly-precipitated carbonate of copper, and this solution mixed with a boiling saturated solution of arsenious acid, a yellowish-green amorphous precipitate is produced, which afterwards becomes crystalline. In this state it has all the properties, and even the fine colour of Schweinfurt-green. According to an analysis by Springmann, this substance has the composition $\text{CuO}, \text{Bu} + 2\text{CuO}, \text{AsO}_3$. It therefore contains 2 atoms of arseniate to 1 atom of butyrate of copper, whilst the corresponding compound with acetic acid contains 3 atoms of the former.—Liebig's *Annalen*, xciv. p. 44.

ANALYTICAL CHEMISTRY.

On the Action of the Air upon the Alkaline Arsenites.

By Dr. C. MOHR.

FRESENIUS has recently called attention to this subject*. I am particularly indebted to him for this observation, as it touches a method of volumetric analysis which I have invented and recommended. In my memoir upon analyses by oxidation and reduction†,

* Chem. Gaz., No. 300, April 16, 1855, p. 148.

† Liebig's *Annalen*, xciii. p. 70.

I had asserted the stability of arsenite of soda. This assertion was then founded upon observations of several months' duration. But Fresenius found that a solution of arsenite of soda, kept in vessels which were not quite full, was "almost entirely" converted into arseniate of soda within three weeks, so that nitrate of silver gave brownish-red precipitates in it. Whilst admitting these observations, I must, on my side, bring forward others of an opposite nature, so that the oxidizability or stability of the alkaline arsenites depends upon circumstances. I have still remaining about $\frac{1}{2}$ a litre out of 2 litres of the same solution of arsenite of soda with which I performed my first experiments; this is now ten months old (No. 1). A second solution was made about six weeks ago (No. 2), and a third quite fresh (No. 3). All the three solutions were prepared from the same arsenious acid, and contain $\frac{1}{10}$ equiv., that is, 4.95 grms. of arsenious acid in the litre. They all contained carbonate of soda in excess.

The fluid which had been kept ten months furnished a fine canary-yellow precipitate with nitrate of silver; there was no intermixture of brown. This was the case with both the other fluids. The three solutions of arsenite of soda were also compared by a solution of iodine in iodide of potassium.

No. 1.—5 cub. centims. of arsenite of soda, ten months old, mixed with starch, required 10.2 cub. centims. of solution of iodine to produce a blue colour. 5 cub. centims., diluted with 200 cub. centims. of water, required 10.2 cub. centims. of solution of iodine. 15 cub. centims., without dilution, required 30.6 cub. centims. of solution of iodine.

No. 2.—5 cub. centims. of arsenite of soda, a month and a half old, required 10.2 cub. centims., and 10 cub. centims. 20.4 cub. centims. of solution of iodine.

No. 3.—5 cub. centims. of freshly prepared arsenite of soda required 10.2, and 10 cub. centims. 20.4 cub. centims. of solution of iodine.

From these experiments, it is very evident that these three fluids, prepared at such different times, were of exactly the same strength; their reactions also gave no indications of arsenic acid. The oldest of my fluids is contained in a large bottle with about $1\frac{1}{2}$ litre of air, and is only lightly closed with a cork.

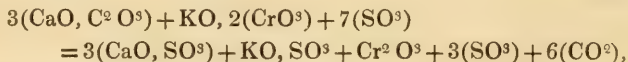
Until the cause of this different behaviour is ascertained, I shall not lose sight of Fresenius's observations. Does the presence of an excess of caustic alkali assist the oxidation, or does arsenious acid exist in different states? It would however in no case be adverse to the applicability of my method. After dissolving the arsenious acid in carbonate of soda, the fluid must be acidulated with sulphuric acid, then diluted to a litre, and supersaturated with carbonate of soda at the moment of employment. In the acid state, arsenious acid can never take up oxygen. But according to my observations above given, I did not find this necessary. The only concession that I have made, consists in dissolving the arsenious acid in nearly its equivalent of bicarbonate of soda. By this means I avoid an excess

of alkali, and even if this were present, it must be in the most inefficient state.

My *solutio mineralis Fowleri* gave a pure yellow precipitate with nitrate of silver, and with magnesia no trace of triple arseniate.—Liebig's *Annalen*, May 1855, vol. xciv. p. 222.

On the Determination of Lime. By H. VOHL.

Lime is usually determined either as carbonate or sulphate. A method which furnishes very exact results consists in precipitating the lime in the form of oxalate, washing the precipitate by decantation, and then treating it in the apparatus of Will and Fresenius with bichromate of potash and sulphuric acid. If a few particles float upon the surface during the decantations, they may be got rid of by the addition of a few drops of æther. The sulphuric acid sets free the oxalic acid of the lime-salt, which is then oxidized by the chromic acid, forming carbonic acid, which is evolved. From this loss the amount of lime is calculated in accordance with the following formula:—



or for 84.396 of lime, 132.000 of carbonic acid will be evolved.

As the washing by decantation requires some practice, and is not always practicable, the oxalate of lime may be filtered and washed; then dissolved on the filter with very dilute boiling muriatic acid. The solution obtained, which may be reduced by evaporation if necessary, is then put into the apparatus for the evolution of the carbonic acid, and after it has been neutralized with ammonia, the chromate of potash is added. In order to prevent any evolution of chlorine, a small quantity of oxide of mercury must be added before the sulphuric acid is added to the mixture.—Liebig's *Annalen*, May 1855, vol. xciv. p. 217.

On the Determination of Mercury by Chloride of Silver.
By Dr. H. VOHL.

When chloride of mercury is treated with sulphuric acid, no decomposition takes place if the temperature does not exceed 212° F.; but every other metallic chloride, with the exception of chloride of silver, is converted into sulphate by this treatment. This behaviour of chloride of mercury renders its determination in mixed metals very easy.

For this purpose the substance is dissolved in nitromuriatic acid, and evaporated to dryness in the water-bath, in the presence of an excess of sulphuric acid. The residue is moistened with water, and the evaporation repeated once or twice, when all the chlorides, except those of silver and mercury, are converted into sulphates. The residue is then dissolved in water and filtered. Acetate of soda

is added to the filtrate, when, if a precipitate which is indicative of the presence of silver is produced, the fluid is to be heated on the water-bath until the precipitate has caked together, and filtered again. A solution of nitrate of silver is then added to the fluid. A precipitate of chloride of silver is produced, which, if the solution was not sufficiently diluted, contains some sulphate of silver, which is difficult of solution, and can be got rid of by washing with boiling water. The addition of acetate of soda must never be neglected, as it is well known that nitrate of mercury dissolves chloride of silver in considerable quantity. The weight of the chloride of silver produced is then ascertained, and from this the amount of mercury is calculated. 101.103 Hg are represented by 143.435 AgCl.

It is clear that by this method the amount of mercury may be just as well determined volumetrically, by previously ascertaining the strength of the silver solution. The result may be checked by washing, drying, and weighing the precipitate of chloride of silver. —Liebig's *Annalen*, May 1855, vol. xciv. p. 220.

PROCEEDINGS OF SOCIETIES.

Royal Society.

May 3, 1855. (Charles Wheatstone, Esq., in the Chair.)

“An Experimental Inquiry into the nature of the metamorphosis of Saccharine Matter, as a normal process of the animal œconomy.”
By Dr. Pavy.

The author begins by observing, that the saccharine matter met with in the animal economy is derived from two sources—from the vegetable kingdom, and from the liver of the animal itself; in each case being poured into the general circulation through the hepatic veins. The liver not only enjoys the power of forming sugar, but it likewise exerts (as shown by the experiments of Bernard) some modifying influence over that which is traversing its capillaries and which has been absorbed from the food, by which it is transformed from *vegetable* into *animal* sugar, and thus rendered more apt for serving in the processes of animal life.

The sugar poured into the general circulation through the hepatic veins is conveyed to the capillaries of the lungs, where it in great part disappears, but never entirely so, according to very numerous analyses which the author has made on this subject. If the blood be traced onwards from the arteries through the systemic capillaries into the veins, the small amount of sugar which impregnates arterial blood will be found to be still undergoing a process of destruction; and what appears exceedingly interesting, this process of destruction is not carried on with equal activity in the different parts of the system at large. In the capillaries of the chylo-poietic viscera, the destruction is so complete, that the blood in the portal vein may be

entirely free from saccharine principle, when the blood returning from other parts, as that contained in the femoral or jugular veins, remains slightly impregnated. This curious fact has a bearing that will be presently adverted to, with reference to the views to be advanced concerning the nature of the metamorphosis of sugar in the animal economy.

The *principal* seat of destruction of saccharine matter in the animal system being located in the respiratory organs, seems at first sight to support the theory of Liebig—that sugar is one of those substances which undergoes a process of combustion, by its direct combination with oxygen and its resolution into water and carbonic acid. Some experiments on the temporary obstruction of the respiration and the examination of arterial blood before and after the operation, led the author to call in question this view, as he observed that notwithstanding the supply of oxygen was cut off to such an extent as almost to occasion death, yet a considerable destruction of sugar took place in the lungs. This, coupled with the fact that a disappearance of sugar takes place in the systemic capillaries, and unequally so in different portions of them, induced him to push his investigations, and see if there might not be some other cause in operation in the living animal to effect the normal destruction of sugar, besides the direct chemical action of the oxygen absorbed in respiration. The results of these investigations, which were first directed towards the changes produced in blood normally containing sugar, injected through the capillaries of lungs removed from the animal, and artificially inflated with atmospheric air or oxygen gas, have induced the author to refer the metamorphosis of sugar in the animal economy, to a process which is perfectly consistent and analogous with the well-known chemical bearings of this substance apart from the animal system.

In experiments which the author has now several times repeated, he injected blood removed from the right side of the heart of an animal—and therefore normally containing sugar—through the capillaries of the artificially inflated lungs of another; and found that as long as the blood retains its fibrine, there is as much destruction of its sugar as would take place in the living animal; but that where the fibrine has been separated from the serum and corpuscles, the sugar ceases to be influenced by the presence of oxygen, or ceases to disappear during this process of artificial respiration. It would hence appear, that something besides mere contact with oxygen is requisite for the destruction of sugar. But in other experiments, he has found that oxygen is nevertheless a necessary agent concerned in the process of transformation observed during the arterialization of the blood that has not undergone spontaneous coagulation. It would therefore seem, in fact, that oxygen acts secondarily on the sugar through the medium of the fibrinous constituent of the blood:—that it exerts some changes upon this azotized principle, which are capable of inducing the metamorphosis of sugar.

If we look to the ordinary chemical bearings of saccharine matter

apart from the animal system, we find that an azotized substance undergoing the molecular changes of decomposition, placed in contact with sugar readily excites a process of fermentation, and converts it by a mere alteration of the grouping of its elements into another substance, one atom of sugar ($C^{12}H^{12}O^{12}$) being resolved into two atoms of lactic acid ($C^6H^6O^6$). We also find that sugar is not susceptible of oxidation except under the influence of strong chemical reagents. Chemical analogy, therefore, would lead us to look upon the secondary action of oxygen as the more probable process of physiological destruction; especially when we take into consideration, that nowhere do we meet with such a constant series of molecular changes taking place as amongst the azotized constituents of a living animal. In the above-mentioned experiment of injecting fibrinated and defibrinated blood through an artificially inflated lung, when the blood is capable of undergoing the molecular changes of assimilation on contact with oxygen as in the living animal, the sugar in great part disappears, but so soon as the fibrine is separated by spontaneous coagulation, and the blood has thus lost its vital characteristics, oxygen is no longer capable of exerting any metamorphosing influence on its saccharine ingredients.

If the molecular changes occurring during the decomposition of an azotized substance be capable of converting sugar into lactic acid, why should not the molecular changes occurring during the building-up or elaboration of this same nitrogenized compound effect the same? Indeed, we have seen that the process of destruction is carried on to a certain extent in the systemic capillaries, and more especially in those of the chylo-poietic viscera, where the molecular changes of nutrition are also correspondingly carried on with greater activity than elsewhere. So that analogy and experiment would tend to show that the physiological destruction of sugar is owing to a process similar to fermentation induced by the molecular changes occurring in the nitrogenized constituents of the animal during life. And, in accordance with this, we find lactic acid present in the system, and largely separated from arterial blood by the muscular tissue, and the discerning follicles of the stomach.

As regards the lactic acid fermentation, it is well known that the presence of an alkali favours, whilst that of an acid retards the process. In two experiments on animals, the author injected carbonate of soda and phosphoric acid into the circulating current, and observed in the case of the latter that sugar immediately accumulated in the blood.

The preceding observations refer more especially to the changes that take place in the saccharine ingredient of the blood during life; and the author next proceeds to notice some interesting phenomena observable during the decomposition, and even the spontaneous coagulation of blood containing sugar.

If the blood of an animal normally impregnated with sugar be placed aside, and allowed to undergo spontaneous coagulation, on examining separately the serum and clot on the following day, it will be found, that although the serum may be largely saturated

with sugar, the clot is entirely, or almost entirely destitute of it. Now, as the clot is moist and remains to a certain extent infiltrated with the serum from which it has partially separated, it would appear that even the molecular changes arising from the spontaneous coagulation of the blood are sufficient to effect the destruction of normal animal sugar. And this conclusion is strengthened by the fact, that in diabetic blood (the sugar of which, as would appear from other considerations also, is not so susceptible of metamorphosis as the healthy variety) the sugar does not disappear to a similar extent in the clot.

Under the changes of the decomposition of blood, normal animal glucose is very readily metamorphosed. The rapidity of the metamorphosis depends on the activity of the decomposition of the animal substances present, and when the destruction of the sugar is complete the blood has assumed an *acid reaction*.

This acid reaction of decomposing blood is only observable in that which was previously pretty largely impregnated with sugar. It appears to be owing to the formation of lactic acid. Certainly, it cannot be due to carbonic acid, for the reaction remains after exposure to a boiling temperature.

The disappearance of sugar in the manner just pointed out does not depend on the oxygen of the air, except in so far as this agent is concerned in exciting the decomposition of the azotized constituents of the blood; for the sugar disappears as rapidly when there is a small, as when there is a large amount of surface exposed to the air. But if the air be carefully and completely excluded, no signs of decomposition of the animal parts of the blood are to be observed, and under these circumstances the sugar also remains. The disappearance of sugar is more rapid where the fibrine and corpuscles are present, than when the serum is exposed alone; and in accordance with this, the blood in the one case undergoes decomposition much sooner than in the other—a fact easily intelligible from the greater amount of azotized ingredients present.

If blood normally impregnated with saccharine matter be placed aside until signs of incipient decomposition are observed, and the sugar is beginning to disappear, exposure to a current of oxygen rapidly completes the total disappearance of the saccharine constituent. In this observation we have a further illustration of the analogy that appears to exist, in the nature of the metamorphosis of sugar as a physiological process, and that which takes place chemically under the influence of an azotized compound, whose elementary particles are in a state of molecular transition. During life, the higher organic constituents of the blood are capable of undergoing the changes of assimilation on exposure to contact with oxygen, and there is a considerable destruction of sugar effected; for a short period after death these azotized constituents remain stationary and uninfluenced by oxygen, and with this, there is a corresponding suspension of the transformation of sugar; but finally, the animal matter of the blood on contact with oxygen, especially during a warm temperature, assumes a state of decomposition, the

molecular changes of which again excite the destruction or metamorphosis of saccharine matter.

The sugar *disappears far less rapidly* from diabetic blood under the influence of exposure to the atmosphere, than from healthy right-ventricular blood. From these, and a few other observations which he has as yet been able to make on the blood in Diabetes Mellitus, the author, were he to hazard an opinion on the nature of that obscure disease, would be disposed to say that there appears to be a modification of sugar produced by the liver, which is not susceptible of undergoing the normal process of destruction in the animal system, and which, therefore, accumulating in the blood, is eliminated by the kidneys. The experiments of Bernard have shown that vegetable glucose (grape-sugar) is not susceptible of destruction in the processes of animal life, unless converted into animal glucose by the agency of the liver. Diabetic sugar would therefore seem to bear a resemblance in its physiological relations to vegetable, rather than to animal glucose.

PATENT.

Patent granted to F. Crace Calvert, for Improvements in the treatment of heating, puddling, and refinery Iron Slags or Cinders.

THE object of this invention is to obtain a better quality of cast and malleable iron from certain iron slags or cinders, known by the names of puddling, refinery and heating slags or cinders, than is effected at the present day. The usual way of applying these slags or cinders on a blast-furnace consists in adding them, either alone or mixed with ironstone, without submitting them to any previous preparation, except sometimes burning them in a heap. The consequence is, that, as they descend in the furnace, they are soon carried to a bright red heat and fused, and get mixed with the various materials which compose the charge of a blast-furnace. A portion of these slags or cinders falling on mine or coke, is not fluxed, and thus gradually finds its way to that part of the furnace where cast iron is being produced, and uniting with it, descends into the cupola or the blast-furnace. It is easy to understand how the above iron slags or cinders, mixing themselves with the cast iron, injure its quality, for iron slags or cinders are chiefly composed of silicate, sulphuret and phosphuret of iron, which act most injuriously on the quality of cast and malleable iron.

The mode of operating, so as to effect the complete fluxing of the above slags or cinders, and thus prevent the silica, sulphur, and phosphorus arriving in contact with the cast iron which is being produced, is as follows:—

The first process consists in reducing the above puddling, refinery, and heating furnace slags or cinders into coarse powder, which is done by any of the ordinary mills and grinding apparatus now in

use, and then adding to them about one-half their weight of slacked lime made into a thick paste. They are then well mixed together, and the mass is made into lumps or bricks of a convenient size, which are dried or not, according to circumstances, previously to adding them at the top of the blast-furnace; or the dried lumps of lime and slag or cinders may be calcined in a separate furnace, and afterwards introduced, with ordinary mine, at the top of the blast-furnace; or the mass of lime and slag may be mixed with coal, coke or charcoal, and calcined in a furnace, or introduced into crucibles, and thus separate the iron which it contains previously to its addition on the blast-furnace. The patentee remarks, that heating slags or cinders generally do not require roasting, but that refinery and puddling slags often do.

The second process consists in roasting or oxidizing the iron slags or cinders before they are mixed with slacked lime. To oxidize these slags or cinders, two different processes are adopted. The slags are reduced to fine powder, and introduced into an oxidizing furnace, such as is used for roasting copper ores; and whilst the powder is carried to a dull red heat, it is well stirred, so as to transform the iron or the protoxide of iron it contains into peroxide, the silicium into silica, the phosphurets into phosphates, and the sulphur into sulphurous acid. When the powder has assumed a bright red colour, and no more sulphurous acid is produced, it is taken out of the furnace and mixed with slacked lime, and applied as above described.

The same purpose is attained by breaking the slags or cinders into small fragments, and introducing them with a small amount of coal into an ordinary kiln, or in one made of four walls which have numerous holes in the sides; the object of which is to admit freely the oxygen of the atmosphere, and which holes are also employed to remove the oxidized slags or cinders. These kilns are worked like ordinary lime-kilns, viz. the slags or cinders, mixed with a small quantity of coal, are constantly added at the top, whilst the oxidized slag or cinder is removed at the bottom by the opening or openings which exist there, and then the prepared slags or cinders are treated with slacked lime, as before described.

The third process to which the patentee submits puddling, refinery or heating slags or cinders, is to reduce them into a powder, and introduce them into furnaces which communicate with the blast-furnace by means of long flues, into which the volatile products given off from the mouths of the blast-furnace or of the coke-oven are passed. When the powdered slags or cinders are not sufficiently heated by the gases for these to act upon the component parts of the slags or cinders, a gentle heat is applied, so as to carry them to a dull red heat; then the silicates of protoxide of iron are decomposed, and metallic iron is produced. When the operation is completed, they are taken out and allowed to cool. Such reduced slags or cinders having been made into powder, are to be treated with slacked lime in manner before described.—Dated August 18, 1854.

THE CHEMICAL GAZETTE.

No. CCCVII.—August 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Devitrification of Glass. By J. PELCZE.

GLASS loses its transparency when, after being fused, it is allowed to cool very slowly, or when it is subjected to a prolonged softening. It becomes converted into a nearly opaque substance, known under the name of *Reaumur's porcelain*. The devitrification of glass must have been known at a very distant period, for it is impossible not to meet with devitrified glass in the crucibles which the glass-makers take out of old furnaces past use. The cooling of such a large mass of masonry is necessarily very slow, so that the remains of glass left in the melting-pots are always placed in favourable conditions for devitrification.

The surface of a mass of fused glass in a melting-pot, and submitted in the furnace itself to a very slow cooling, becomes covered with a more or less thick and opaque crust, whilst in the central parts there are groups of acicular crystals springing from a common centre, and forming balls or granulations suspended in a transparent mass.

Reaumur, who repeatedly turned his attention to devitrification, devoted his researches more particularly to the means of producing it in a complete manner. The following is a brief description of his process. The glass objects which are to be converted into porcelain are to be placed in large crucibles. The objects, and all the spaces between them, are to be filled with a mixture of fine white sand and gypsum, and this in such a manner that they may neither touch each other nor the sides of the crucible. The latter is then covered, luted, and put into a place where the action of the fire is strong. When taken out and opened (Reaumur does not say after how long), all the objects contained in it will be found converted into a fine white porcelain.

Reaumur considered calcined gypsum as one of the most proper materials for the conversion of glass into white porcelain. He attributed the same property to sand, and added, that very white sand, such as that of Etampes, furnished with gypsum a compound powder, which was preferable to gypsum or sand alone.

Reaumur thought that the arts would soon take advantage of devitrification to obtain a new porcelain. His first attempts were made in 1727, his last in 1739, and since then it has several times been attempted to introduce his porcelain; it has been employed for bottles, tiles for floors, mortars, vases of different forms, and cap-

sules and tubes for particular chemical operations; but experience has not yet realized Reaumur's expectations. Two circumstances stand in the way of the industrial, that is to say æconomical, fabrication of objects in devitrified glass, namely, the necessity of subjecting these objects to a prolonged softening, which is a considerable obstacle to the preservation of their form; and secondly, the length of the operation, which necessitates considerable expense in combustibles and labour. I think, however, that it will be possible to produce plates of devitrified glass of considerable size, simulating fine porcelain, and capable of replacing it in certain cases. These plates, although very hard, may be rendered smooth and polished like plate-glass.

The chemical phænomena of the devitrification of glass do not appear to have been closely studied. M. Dumas having made a comparative analysis of a crystalline glass, and of another which was amorphous and transparent, both taken from the same melting-pot, considered the former to be a definite compound, richer in silica and containing less alkali than the latter, and consequently less fusible. Starting from this analysis, the results of which were incontestable, and which besides tallied with the opinions of Berthollet upon the crystals observed in glass by Keir, M. Dumas considered devitrification as a crystallization of glass, due to the formation of definite compounds, infusible at the actual temperature of the moment of devitrification. He admits that this relative infusibility is the result sometimes of the volatilization of the alkaline base, sometimes of a simple separation of the elements of the glass, the alkalies in this case passing into the portion which retains its glassy state. Some chemists, however, with Berzelius at their head, have given a different opinion, which is adopted by the glass-makers in general, regarding Reaumur's porcelain as nothing but crystallized glass. The facts here brought forward corroborate this view, and appear to show that the crystallized glass which was the subject of the experiments of M. Dumas must have been produced under very exceptional conditions.

Glass, in becoming devitrified, undergoes no alteration either in its nature or in the proportion of the substances of which it is composed. The crystals agglomerated in the form of balls, isolated from one another in a mass of transparent glass, do not differ from the latter in their composition. This is the result of a great number of analyses.

Chemical analysis is corroborated in this case by a physical observation of no less certainty. If a change of composition took place in a mass of glass when slowly cooled, it would leave traces of its existence in the form of bubbles, streaks, or some other sign of heterogeneity; but the brilliancy, transparency, and homogeneity of the unmodified portions are perfect.

The most simple and decisive experiment to show that the devitrification of glass is a simple physical change, consists in keeping some weighed glass plates upon the sole of an annealing furnace until the devitrification is complete, which usually takes place in

twenty-four, or at the outside forty-eight hours. Their weight remains constantly the same; and if white glass of fine quality be employed, it is absolutely impossible to distinguish anything but crystals in the devitrified mass. By fusion, these crystals furnish a transparent glass, identical in composition with that from which they were produced. When poured upon a casting table, and rolled into the form of a piece of plate glass, this glass may be devitrified a second time by a prolonged softening. The same experiments of fusion and crystallization were repeated a third time, without the least change in the composition or weight of the glass.

The easiest and most simple method of preparing devitrified glass consists in subjecting to a prolonged softening a sheet of window glass or a piece of plate glass. The time varies according to the nature of the glass and the temperature, but the devitrification is generally complete in between twenty-four and forty-eight hours. The plate resembles a piece of porcelain, but may easily be distinguished when broken. It is found to be composed of opaque, slender, close needles, lying parallel to each other and perpendicular to the surface of the glass. If the plate be taken out of the furnace before the devitrification is complete, the crystallization is always observed to commence from the surfaces and to proceed slowly to the centre, so that a sheet of transparent glass still exists in the interior of the plate. The point of union of the crystals is marked by a line, which is usually very visible even in completely devitrified specimens, and along this line there are sometimes crystalline nuclei. In some rare cases the fibrous texture disappears, and the devitrified glass presents to a certain extent the saccharoid fracture and the aspect of a fine white marble; sometimes also the crystals disappear, and are replaced by a substance which might be taken for enamel.

Window glass, and especially bottle glass, when devitrified in large masses in crucibles, occasionally presents the form of greenish-yellow needles, which are sometimes small and short, but sometimes more than a centimetre in length, strongly adherent to one another and interlacing in every direction, but leaving vacant spaces, which give them a certain resemblance to crystallizations of sulphur.

Devitrified glass is a little less dense than transparent glass; its hardness is considerable, for it scratches the latter with ease and strikes fire with steel. Although brittle, it is much less so than ordinary glass, and it is a bad conductor of heat. A plate of devitrified glass is a conductor of ordinary electricity. It possesses this property nearly in the same degree as marble, and to a much greater degree than common glass and porcelain.

It was supposed that devitrified glass was nearly infusible, and that tubes formed of this substance would behave nearly like those of porcelain when exposed to high temperatures. On the contrary, devitrified glass fuses almost as readily as the amorphous glass from which it is produced; it appears however that crystallized glass is more refractory than ordinary glass.

All the glasses found in commerce, plate, window and bottle glass, may be devitrified. Even crystal glass, notwithstanding Reaumur's

assertion to the contrary, is no exception; it is devitrified without any separation of the oxide of lead which it contains. It acquires the appearance of porcelain, but its fracture is smooth and homogeneous, without the fibrous texture, as is also sometimes the case in the ordinary glasses with soda and potash bases.

The potash glasses, such as those of Bohemia, undergo devitrification with much greater difficulty than the soda glasses. Borosilicate of potash and lime, exposed for four days in the hottest part of a spreading-oven, was not devitrified, although the temperature was sufficiently high to soften this glass. Under the same conditions, the borosilicate of potash and zinc showed some signs of devitrification. The silicate which devitrifies with the greatest ease, is the trisilicate of soda, $\text{NaO}(\text{SiO}_3)_3$. Small crucibles are sometimes completely filled with a confused crystallization of this glass, although there was no intention of producing it; and when a transparent mass of trisilicate of soda is annealed, it acquires a very peculiar opaline appearance, at a temperature far below that necessary for devitrification.

Devitrification appears to be rendered far more easy by the introduction of refractory matters, or such as are difficult of fusion in the pasty glass, such as ashes, sand, and, which is very singular, the glass itself finely powdered, or by the mixture of substances of which it is composed.

The following experiment, made with more than 100 kilogrms. of glass, proves the correctness of this assertion. Two pots, half filled with fused glass, were left in a furnace, which was then allowed to cool; and when the substance had become pasty, a *very small quantity* of vitrifiable matter was added to one of the pots. The furnace having then been allowed to cool slowly, the two pots were taken out, when that to which nothing had been added contained a transparent glass, in which devitrification had scarcely commenced, whilst that in the other was almost entirely opaque, and filled throughout with crystalline nuclei. 1 or 2 per cent. of sand are sufficient to induce this change in a mass of glass, provided the temperature of the latter be not too high, which may readily be ascertained from the slight fluidity of the substance.

Quartz, exposed to the action of heat under the conditions which induce the devitrification of glass, retains its transparency. It appears that to produce the phenomenon of devitrification, a heat sufficient to soften the substances submitted to experiment is necessary. This condition cannot be fulfilled with quartz.

The author has devitrified the following coloured glasses:—

Blue cobalt glass,
Green chrome glass,
Blue copper glass,
Yellow charcoal glass,
Black iron glass;

and these different glasses exhibit the same behaviour as white glass.

At the conclusion of M. Pelouze's memoir, M. Dumas made some observations in support of his own views. He says that although it may be true that a mass of glass may be completely converted into crystals, and that the *mass* may have the same composition as the transparent glass from which it was produced, it by no means follows that the crystals do not differ in composition in the same mass, and that this indeed is what might be expected, as glasses, instead of being definite and homogeneous compounds, are mixtures of different silicates united into a mass by fusion. But in crystallizing, the less fusible silicates will be the first to separate, as is the case in alloys; so that he considers that in a mass of devitrified glass, crystals of perfectly distinct silicates may exist side by side.

He states that in the analysis of a devitrified window glass, he found 64.7 of silica in the vitreous, and 68.2 in the crystallized portion. M. Leblanc, also, in a mass of plate glass, found 66.2 of silica in the transparent, and 69.3 in the crystallized part. In bottle glass he found 57.9 of silica in the transparent, and 62.95 in the crystallized portion. In this glass it was remarkable that the vitreous portion contained 1.57 of protoxide of iron, whilst the crystals only contained undeterminable traces.

M. Dumas compares the masses obtained by M. Pelouze with those produced by the mixture of several fatty acids. When fused, they constitute a homogeneous liquid; but on solidifying they form a fibrous masses, in which, although the eye can detect no dissimilarity, each acid is nevertheless separated in distinct crystals.—*Comptes Rendus*, June 25, 1855, p. 1321.

On a new Class of Organic Radicals. By ADOLPHE WURTZ.

The organic groups which are admitted by chemists to exist in the alcohols and æthers have been isolated by Kolbe and Frankland. By submitting the volatile fatty acids, $C^n H^n O^+$, to electrolysis, and decomposing the hydriodic æthers by zinc, these chemists have ascertained the existence of a series of carbonated hydrogens, the composition of which is represented by the following formulæ:—

$C^2 H^3$, methyle.

$C^4 H^5$, æthyle.

$C^8 H^9$, butyle.

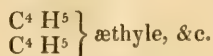
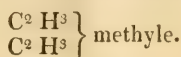
$C^{10} H^{11}$, amyle.

Caproyle, $C^{12} H^{13}$, has since been added to this series.

It is seen, according to Kolbe and Frankland, that the alcoholic radicals retain, when free, the atomic weight and molecular form which they affect in their combinations. Such as they exist in the alcohols, they are when isolated; and in this state their equivalent corresponds to 2 vols. of vapour. This opinion has not been adopted by all chemists. MM. Laurent and Gerhardt were the first to propose to double the formulæ of the alcoholic radicals. The comparison of the boiling-points of these compounds led Hofmann to an analogous conclusion: but his argument, founded upon physical

data, has not been accepted by Kolbe, who has pointed out that the law of the boiling-points does not appear to him to be applicable to compounds of which the equivalent corresponds with 2 vols. of vapour. However this may be, it has appeared to me that it would be useful to bring into this discussion some new arguments, drawn from indisputable chemical facts.

Let us first lay down the question, and settle what is to be understood by the double formulæ under consideration. These formulæ represent binary groups, double molecules, each formed by 2 equivs. of the radicals, such as they exist in the alcohols. They indicate that at the moment of their being set free, the alcoholic groups combine, as it were, with one another, so as to form the compounds,—



When put in this manner, the question of the radicals affects one of the most important and delicate of chemical doctrines; and this will explain the interest which attaches to every fact capable of throwing some light upon this discussion. The following is my argument:—

If the radicals, when free, constitute double molecules, we should be able to replace an alcoholic group by some other in these molecules, and thus obtain a series of mixed radicals. If æthyle is formed by two æthylic groups, we should be able to substitute for one of these groups the radical of butylic or amylic alcohol, so as to form by this substitution the mixed radicals æthylobutyle, æthyloamyle, &c. These radicals do really exist, and I have obtained them under two different circumstances:—

1. By decomposing a mixture in atomic proportions of two hydriodic æthers by means of sodium; and

2. By the electrolysis of a mixture of fatty acids.

When a mixture of iodide of æthyle and iodide of butyle is treated with a proportionable quantity of sodium, there is formed, independently of some secondary products, iodide of sodium, æthyle, butyle, and a compound of these two radicals, that is to say, the mixed radical *æthylobutyle*, $\left. \begin{array}{l} \text{C}^4 \text{H}^5 \\ \text{C}^3 \text{H}^9 \end{array} \right\}$. Æthyle is gaseous; æthylobutyle is a light and mobile liquid, which boils at $143^{\circ}6 \text{ F.}$, and is easily separated from the butyle, which only boils at $222^{\circ}8 \text{ F.}$

Æthyloamyle, $\left. \begin{array}{l} \text{C}^4 \text{H}^5 \\ \text{C}^{10} \text{H}^{11} \end{array} \right\}$, is formed under the same circumstances, by the decomposition of a mixture of iodide of æthyle and iodide of amyle by means of sodium. As its boiling-point is $190^{\circ}4 \text{ F.}$, it is easily separated by fractional distillation from the amyle, which boils at $316^{\circ}4 \text{ F.}$ It possesses the power of rotation to the right, like amyle itself, a circumstance which appears to indicate that the amylic radical exists in it without alteration.

I have obtained *butyloamyle*, $\left. \begin{smallmatrix} \text{C}^8 & \text{H}^9 \\ \text{C}^{10} & \text{H}^{11} \end{smallmatrix} \right\}$, by decomposing a mixture of iodide of butyle and iodide of amyle by sodium.

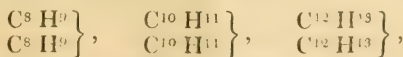
Butylocaproyle, $\left. \begin{smallmatrix} \text{C}^8 & \text{H}^9 \\ \text{C}^{12} & \text{H}^{13} \end{smallmatrix} \right\}$, containing at once the radicals of butylic and caproic alcohols, was obtained by the electrolysis of a mixture of valerate and cœnanthylate of potash. As it boils about 311°F. , it was easily separated from the butyle, boiling at $222^\circ\cdot 8 \text{ F.}$, and from the caproyle, boiling at $395^\circ\cdot 6 \text{ F.}$, which are formed simultaneously with it.

The circumstances under which these mixed radicals are formed, and their physical properties, amongst which we may particularly notice the rotatory power of æthyloamyle, throw a great light upon their constitution. Moreover, the comparison of their properties with those of the normal radicals, leaves no doubt as to the place occupied by the latter in the series, and consequently as to their true equivalent. The following table will show these.

Table of the Physical Properties of the Alcoholic Radicals.

Radicals.	Composition.	Density at 32°F.	Density of vapour.		Boiling-point.
			Observed.	Theory.	
Æthylobutyle ...	$\text{C}^{12} \text{H}^{14} = \left\{ \begin{smallmatrix} \text{C}^4 & \text{H}^5 \\ \text{C}^8 & \text{H}^9 \end{smallmatrix} \right\}$	0·7011	3·053	2·972	$143^\circ\cdot 6 \text{ F.}$
Æthyloamyle	$\text{C}^{14} \text{H}^{16} = \left\{ \begin{smallmatrix} \text{C}^4 & \text{H}^5 \\ \text{C}^{10} & \text{H}^{11} \end{smallmatrix} \right\}$	0·7069	3·522	3·455	$190^\circ\cdot 4 \text{ F.}$
Methylocaproyle ?	$\text{C}^{14} \text{H}^{16} = \left\{ \begin{smallmatrix} \text{C}^2 & \text{H}^3 \\ \text{C}^{12} & \text{H}^{13} \end{smallmatrix} \right\}$		3·426	3·455	$179^\circ\cdot 6 \text{ F.}$
Butyle	$\text{C}^{16} \text{H}^{18} = \left\{ \begin{smallmatrix} \text{C}^8 & \text{H}^9 \\ \text{C}^8 & \text{H}^9 \end{smallmatrix} \right\}$	0·7057	4·070	3·939	$222^\circ\cdot 8 \text{ F.}$
Butyloamyle	$\text{C}^{18} \text{H}^{20} = \left\{ \begin{smallmatrix} \text{C}^8 & \text{H}^9 \\ \text{C}^{10} & \text{H}^{11} \end{smallmatrix} \right\}$	0·7247	4·465	4·423	$269^\circ\cdot 6 \text{ F.}$
Amyle	$\text{C}^{20} \text{H}^{22} = \left\{ \begin{smallmatrix} \text{C}^{10} & \text{H}^{11} \\ \text{C}^{10} & \text{H}^{11} \end{smallmatrix} \right\}$	0·7413	4·956	4·907	$316^\circ\cdot 4 \text{ F.}$
Butylocaproyle ...	$\text{C}^{20} \text{H}^{22} = \left\{ \begin{smallmatrix} \text{C}^8 & \text{H}^9 \\ \text{C}^{12} & \text{H}^{13} \end{smallmatrix} \right\}$		4·917	4·907	$311^\circ\cdot 0 \text{ F.}$
Caproyle	$\text{C}^{24} \text{H}^{26} = \left\{ \begin{smallmatrix} \text{C}^{12} & \text{H}^{13} \\ \text{C}^{12} & \text{H}^{13} \end{smallmatrix} \right\}$	0·7574	5·983	5·874	$395^\circ\cdot 6 \text{ F.}$

From this table it is seen that the numbers expressing the composition, the densities of vapour, and the boiling-points of the normal and mixed radicals, follow a nearly regular progression, and establish a sort of harmony between the composition on the one hand and the physical properties on the other. Now this harmony is very natural, and may be easily explained if we adopt for butyle, amyle, and caproyle the double formulæ—



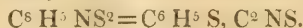
whilst it would be disturbed if we attributed to these radicals the simple formulæ—



Comptes Rendus, June 18, 1855, p. 1285.

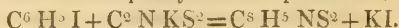
*On the artificial Production of the Essential Oil of Mustard.**By MM. BERTHELOT and DE LUCA.*

The authors refer to the investigations of many chemists for the last thirty years upon the nature of essence of mustard, and especially to the researches of MM. Dumas and Pelouze, who in 1833 analysed it, determined the density of its vapour and its principal properties, and discovered the finely-crystalline body thiosinamine, prepared by the action of ammonia upon the oil of mustard; and to those of M. Wertheim, who has shown that this essence, $C^8 H^5 NS^2$, may be regarded as a compound of oil of garlic, $C^6 H^5 S$, with hydrosulphocyanic acid,—



Upon the preceding data the authors proceeded to obtain essence of mustard without the aid of any substance derived from cruciferous plants, by taking glycerine as a starting-point. In a recent memoir*, they showed that glycerine treated with iodide of phosphorus furnished iodized propylene, $C^6 H^5 I$. The formula of essence of garlic, $C^6 H^5 S$, only differing from that of iodized propylene in the substitution of sulphur for the iodine, all that was necessary was to effect this substitution, and then to combine the product with hydrosulphocyanic acid, in order to produce oil of mustard.

This double reaction was effected at a single operation by treating iodized propylene with sulphocyanide of potassium,—



The reaction is completed in a few hours at $212^\circ F.$ in a close vessel; essence of mustard and iodide of potassium are the principal products obtained.

The liquid produced possesses the known properties of essence of mustard; it exerts the same irritating action upon the eyes and skin, boils at the same temperature, and when treated with ammonia furnishes thiosinamine in the same manner,—



The composition of thiosinamine thus prepared is,—

	Found.		Calculated.
C	40.9	8	41.4
H	7.0	8	6.9
N	23.0	2	24.1
S	28.0	2	27.6

This thiosinamine agrees in composition, properties, and crystalline form with that obtained from the natural essence.

This origin of essence of mustard from iodized propylene, a derivative of glycerine, shows that essence of garlic may be derived from propylene, $C^6 H^6$, one of the carburets corresponding with the alcohols; essence of garlic is sulphuretted propylene, and essence of mustard is sulphocyanide of sulphopropylene. This result will no doubt lead to the production of similar compounds from other car-

* Chem. Gaz., No. 291, Dec. 1, 1854, p. 448.

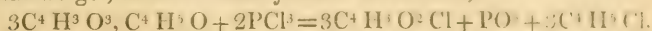
burets homologous with propylene, especially from olefiant gas; and the authors intend making some experiments in this direction.

They add, that from the relation between glycerine and essence of mustard established by their experiments, it appears that the latter may be formed by means of the neutral fatty substances, which are so abundant in vegetables, and especially in the Cruciferae; this will probably throw some light upon the origin of the natural essence.—*Comptes Rendus*, July 2, 1855, p. 21.

Researches on the Constitution of the Æthers. By M. BÉCHAMP.

In a note read before the Academy on the 23rd of April*, I have shown that monohydrated acetic acid behaves with protochloride of phosphorus like a mixture of water and anhydrous acetic acid; in other words, that under these conditions this acid must be considered as acetate of oxide of hydrogen. In the same note I have approximated to alcohol the æthers of the monobasic acids considered as salts of oxide of æthyle, and to monohydrated acetic acid the double anhydrides of M. Gerhardt. The present paper is intended to verify this approximation by experiment, to prove that alcohol may really, in certain cases, be regarded as a hydrate, and the æthers as salts of oxide of æthyle, or of hydrate of bicarbonated hydrogen.

If the constitution of the saline æthers is that which the theory of æthyle attributes to alcohol, and which I have endeavoured to establish for the monohydrated acids, these æthers must furnish with protochloride of phosphorus, chloride of æthyle and the chloride of the radical of the organic acid. I have made the experiment with acetic æther. Very pure and very dry acetic æther, boiling at $165^{\circ}2$ F., mixes in all proportions with protochloride of phosphorus; the temperature is scarcely raised during the mixture. In the cold or at 212° F. no reaction takes place in a sealed tube; but between 320° and 356° F. the tube acquires a coat of phosphorous acid, and when the reaction has lasted twenty-four hours the transformation is nearly complete. The liquid which remains in the tube is perfectly colourless. I have ascertained that this liquid is only a mixture of hydrochloric æther and chloride of acetylc, with a little unaltered materials. No muriatic acid is produced in the reaction. Thus we get, as with monohydrated acetic acid,—

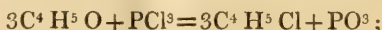


I shall hereafter describe how I easily ascertained the formation of the hydrochloric æther. As to the chloride of acetylc, I determined that its boiling-point was 131° or $131^{\circ}6$ F., and that it presented all the characters of a pure product.

I have proved that anhydrous acetic acid is converted into chloride of acetylc by protochloride of phosphorus. Common æther, under the same circumstances, undergoes the same kind of reduction. M. Jaquemin and myself have effected this conversion. Anhydrous æther mixes with protochloride of phosphorus in all

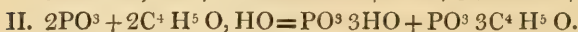
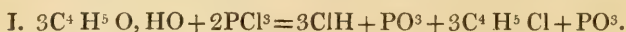
* Chem. Gaz., No. 303, June 1, 1855, p. 212.

proportions without a sensible increase of heat; the presence of water or alcohol, in quantities however small, causes the mixture to take place with an extremely violent reaction. We operated with very pure and dry æther. The reaction of the two liquids only takes place between 356° and 392° F. After it had lasted twenty hours, the tube was covered with a thick crust, and the hydrochloric æther, which was formed abundantly, escaped with rapidity if the tube was opened without care,—



only that, from the high temperature at which the double decomposition is effected, the phosphorous acid is partially decomposed, so that the solid mass which clothes the tube is a mixture of phosphorous acid, phosphoric acid and red phosphorus. We did not observe muriatic acid amongst the products of the reaction.

We have also resumed the examination of protochloride of phosphorus upon absolute alcohol. The chloride, on falling into the alcohol, reacted with remarkable violence, although the retort was kept in a freezing mixture. Our observations were as follows:—At the first moment an unequivocal evolution of muriatic acid took place; this afterwards ceased, but recommenced as soon as the apparatus was heated. The disengagement of muriatic acid was very abundant, and the quantity of hydrochloric æther very considerable. When the residue in the retort was distilled, a very foetid liquid was obtained of an alliaceous odour; it was the phosphorous æther of Williamson. Lastly, the retort contained hydrated phosphorous acid. We conceive the reaction to take place as follows:—



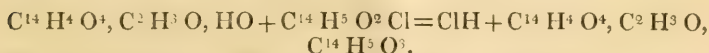
But the quantity of this phosphorous æther is always very inconsiderable, a few grammes passing about 374° F. from 100 grms. of alcohol; this is because, notwithstanding the evolution of muriatic acid, a portion of this acid assists in the ætherification of the alcohol.

To prove the formation of hydrochloric æther, we were not contented with ascertaining that this body burnt with a green flame, and that its boiling-point was $51^{\circ}8$ F.; we converted it into hydrosulphuric æther, and this into the compound obtained by M. Loir, by combining it with bichloride of mercury. This compound, from its insolubility in water, allows the recognition of traces of hydrosulphuric æther, and even of very slight traces of hydrochloric æther.

From these experiments it appears to me that we may conclude that alcohol and the æthers of the monobasic acids are compounds of the same order, and formed by the union of oxide of æthyle with the anhydrous acid, since each of the compounds supposed to exist in them behaves as it would do if it were isolated. Moreover, the mode of condensation of the elements in alcohol and in these compound æthers is the same; and it appears that the 2 vols. of vapour of oxide of æthyle and the 2 vols. of vapour of water, or of the an-

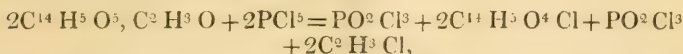
hydrous acid, were united without condensation, as may be observed generally when two gases combine in equal volumes.

The action of protochloride of phosphorus on the æthers, and the discovery of the bibasic nature of salicylic acid, do away with the anomaly presented by the essence of *Gaultheria procumbens*. The essence of *Gaultheria* becomes salicylomethylic acid and the æthylic compound, salicylovinic acid. Anhydrous salicylic acid would be $C^{14} H^4 O^4$, the *salicylide* of M. Gerhardt; methylsalicylic æther or salicylomethylic acid would be $C^{14} H^4 O^4$, $C^2 H^3 O$, HO, and the salicylomethylates $C^{14} H^4 O^4$, $C^2 H^3 O$, MO. If this be correct, nothing is more simple than the explanation, in accordance with the theory of Lavoisier, of the formation of the benzoate of methylsalicyle for example, which was obtained by M. Gerhardt by the action of chloride of benzoyl upon oil of *Gaultheria*, as well as the evolution of muriatic acid, which is the consequence of it; thus,—



Anhydrous benzoic acid replaces the hydrogen of the water disengaged as muriatic acid.

As to the chloride of methylsalicyle, it could not be produced. M. Gerhardt, in fact, has proved that perchloride of phosphorus converts essence of *Gaultheria* into chloride of methyle and chloride of salicyle, which is explicable thus:—



a reaction identical with that which I have already described, and through which acetic æther becomes converted into chloride of æthyle and chloride of acetylene, only as $C^{14} H^5 O^5$ still contains hydrogen in the form of water, muriatic acid is evolved at the same time. As to the question why $C^{14} H^5 O^5$, which is also $C^{14} H^4 O^4$, HO, does not evolve the whole of its water in the form of hydrochloric acid, it is the same as this,—Why does not æther, which is the hydrate of bicarbonated hydrogen, do the same in the presence of PCl^5 ? These are questions which I shall endeavour to solve by the examination of the bibasic and vinic acids, in the direction of the investigations which I have undertaken upon the monobasic acids and their æthers.—*Comptes Rendus*, July 2, 1855, p. 23.

On the Oxides $R^2 O^3$. By Prof. ROCHLEDER.

In a memoir communicated last year to the Academy of Sciences of Vienna, the author put forward the three following opinions with regard to the constitution of organic compounds:—

1. The more highly compound radicals are produced from less compound radicals by substitution, the hydrogen being replaced by other radicals.

2. The nature of a compound depends upon that of the radical. If the radical be electro-positive, the compound with oxygen is a

basic oxide; if it be electro-negative, the compound with oxygen is an acid.

3. If a compound containing an electro-positive radical contains 1, 2, or 3 equivs. of oxygen combined with the radical, the oxide is a monoacid, biacid or triacid base; or if an electro-negative radical contains 1, 2, or 3 equivs. of oxygen, the oxide is a monobasic, bi-basic, or tribasic acid.

In the present memoir the author treats of the metallic oxides, containing 2 equivs. of metal and 3 equivs. of oxygen, which stand so strongly in opposition to many views in organic chemistry, that it has been necessary to raise hypotheses upon these oxides, in order to bring their constitution into agreement with that of other bodies. Thus Gerhardt, as is well known, ascribes two different atomic weights to such metals.

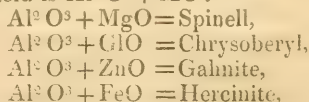
The analysis of the salts formed with acids by the oxides $R^2 O^3$ has shown, that when the acid is monobasic and the salt neutral, they are constituted according to the formula $R^2 O^3 + 3S'$, in which S' indicates a monobasic acid. The formula $2(R^2 O^3) + 3S''$ expresses the constitution of the neutral salts of these bases with a bibasic acid, which is indicated by the sign S'' . The neutral salts of these oxides with a tribasic acid are represented by the formula $R^2 O^3 + S'''$.

When thus indicated, the constitution of these salts agrees with the rule above laid down, that the sum of the equivalents of oxygen combined with the radical in the base is equal to the sum of those combined with the radical in the acid. Consequently the radical of these oxides, such as alumina, oxide of iron, oxide of chrome and oxide of manganese, is a double atom of the metal, which is therefore an electro-positive radical.

All these oxides also possess the faculty of combining with the oxides of alkaline metals, the oxides of the metals, the alkaline earths, &c., forming compounds in which the oxides $M^2 O^3$ take the place of acids. This fact might apparently militate against the rule proposed, and the author has consequently been induced to investigate these compounds more closely.

Whilst the neutral salts in which $M^2 O^3$ acts as a base, contain 3 equivs. of a monobasic acid, the compounds in which $M^2 O^3$ acts the part of an acid only contains 1 equiv. MO as base.

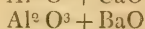
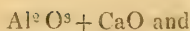
No oxide ($M^2 O^3$) has a greater number of known compounds of this kind than alumina, $Al^2 O^3$. The formula of the salts in which alumina acts as an acid is $Al^2 O^3 + MO$:—



are examples of salts occurring in nature in which alumina acts the part of a monobasic acid.



were prepared by Unverdorben and Fremy.



were obtained by precipitating $\text{Al}^2\text{O}^3 + \text{K}_2\text{O}$ with chloride of calcium and chloride of barium. 51.4 of alumina expel 22.6 of carbonic acid from an excess of carbonate of soda, so that $2\text{Al}^2\text{O}^3$ expel C^2O^2 ; the compound of alumina and soda must therefore consist of $\text{Al}^2\text{O}^3 + \text{NaO}$.

The hydrate of alumina which corresponds to these compounds is diaspore = $\text{Al}^2\text{O}^3 + \text{HO}$. Diaspore is insoluble in muriatic acid; it is not the hydrate of the *base* alumina, but of the *acid* alumina, which possesses little affinity for acids, but which may be converted into basic alumina only by the action of strong acids.

The hydrate of basic alumina is $\text{Al}^2\text{O}^3 + 3\text{HO}$; it is obtained by precipitation with ammonia from a solution of alumina in muriatic or nitric acid, and consequently from a solution in which the alumina was contained as base. This hydrate is soluble in acids. Gibbsite = $\text{Al}^2\text{O}^3 + 3\text{HO}$, is also a hydrate of basic alumina; unlike diaspore, it is soluble in acids. The so-called plombgomme = $(\text{PO}^5 + 3\text{PbO}) + 6(\text{Al}^2\text{O}^3 + 3\text{HO})$ is also soluble in acids.

If we hold fast to the principle, that in a neutral salt the acid and the base contain an equal number of equivalents of oxygen in addition to the radical, it follows that the acid alumina must contain a different radical from the basic alumina; that the acid alumina must consist of a radical, Al^2O^2 , combined with 1 equiv. of oxygen. But when alumina acts as a base, it contains Al^2 combined with 3 equivs. of oxygen.

Alumina is therefore Al^2O^3 , a triacid base. $\text{Al}^2\text{O}^2, \text{O}$ is alumina as a monobasic acid. The radical Al^2 is electro-positive; the compound with oxygen is consequently a base. The radical Al^2O^2 is electro-negative; hence the compound with 1 equiv. of oxygen is an acid, and this is monobasic, because it only contains 1 equiv. of oxygen in addition to the radical. The behaviour of the oxides of iron, manganese, and chrome is exactly like that of alumina. Oxide of iron heated with carbonate of soda, expels so much carbonic acid, that for 2 equivs. of Fe^2O^3 , 1 equiv. C^2O^2 is produced. The compound therefore contains $\text{Fe}^2\text{O}^3 + \text{NaO}$. That the compounds of oxide of iron in which it plays the part of an acid are analogous in their composition to those of alumina, is evident from the circumstance, that in compounds in which alumina acts as an acid, it may be displaced by oxide of iron.

Chlorospinelle is $12\text{MgO} + \begin{cases} 11\text{Al}^2\text{O}^3 \\ 1\text{Fe}^2\text{O}^3 \end{cases}$, one-twelfth of the alumina in the compound $\text{Al}^2\text{O}^3 + \text{MgO}$ being replaced by oxide of iron. If the alumina in spinelle be $\text{Al}^2\text{O}^2, \text{O}$, the oxide of iron in chlorospinelle must be $\text{Fe}^2\text{O}^2, \text{O}$, whilst in the persalts of iron it is Fe^2O^3 , that is to say, oxide of iron is a triacid base and a monobasic acid. The radical of the base is a double atom of iron, and consequently electro-positive; the radical of the oxide as acid is a compound of an electro-negative radical, Fe^2O^2 .

Corresponding hydrates are known,—a hydrate $\text{Fe}^2\text{O}^2 + \text{HO}$

= $\text{Fe}^2 \text{O}^3$, $\text{O} + \text{HO}$, and a hydrate $\text{Fe}^2 \text{O}^3 + 3\text{HO}$. Several bog-iron ores are compounds, or perhaps mixtures, of the two hydrates; thus the hydrate $2(\text{Fe}^2 \text{O}^3) + 3\text{HO}$ may be regarded as $(\text{Fe}^2 \text{O}^3 + 3\text{HO}) + 2(\text{Fe}^2 \text{O}^3, \text{O} + \text{HO})$, the hydrate $\text{Fe}^2 \text{O}^3 + 3\text{HO}$ as $(\text{Fe}^2 \text{O}^3, \text{O} + \text{HO}) + (\text{Fe}^2 \text{O}^3 + 3\text{HO})$. Franklinite is $\text{ZnO} + \text{Fe}^2 \text{O}^3, \text{O}$. It is isomorphous with spinelle, a part of its oxide of zinc being replaced by protoxide of iron and manganese. A part of the oxide of iron is replaced in Franklinite by oxide of manganese = $\text{Mn}^2 \text{O}^3$, whence it follows that oxide of manganese may occur as an acid, and must then, like oxide of iron, be regarded as $\text{Mn}^2 \text{O}^3, \text{O}$.

Oxide of chrome furnishes several hydrates, which however do not throw much light on the question; the compound of oxide of chrome with lime, in which the oxide of chrome acts as an acid, is basic like the compound of oxide of iron with lime, which was prepared like the chrome compound by Pelouze. On the other hand, the chrome-iron ore explains the nature of oxide of chrome as an acid. This mineral is $\text{Cr}^2 \text{O}^3 + \text{FeO}$. The oxide of chrome is partially replaced by alumina, as on the other hand the protoxide of iron by magnesia. Oxide of chrome must consequently be regarded exactly like alumina in this compound, as $\text{Cr}^2 \text{O}^2, \text{O}$. The same constitution must be attributed to the oxide of chrome in the compound $\text{Cr}^2 \text{O}^3 + \text{MgO}$, which was obtained artificially by Ebelmen crystallized in octahedra.

Thus if we examine the compounds of one of these metals with oxygen, as for instance iron, we have in the protoxide, FeO , a mono-acid base, the radical Fe being electro-positive; and in the basic peroxide a triacid base, the radical Fe^2 being electro-positive. The protoxide is monoacid, the peroxide triacid, because the former contains 1, the latter 3 equivs. of oxygen in addition to the radical. Peroxide of iron as an acid is a monobasic acid, because it contains 1 equiv. of oxygen in addition to the radical, and the radical $\text{Fe}^2 \text{O}^2$ is electro-negative from its containing oxygen.—*Sitzungsber. der Akad. der Wiss. zu Wien, Math. Naturwiss. Cl.*, xv. p. 364.

ANALYTICAL CHEMISTRY.

On a Method of Analysis for Bronze and Brass.

By H. SAINTE-CLAIRE DEVILLE.

I HAVE for some years caused the pupils of the Ecole Normale, in my laboratory, to make use of a method of analysis for bronzes and brasses, which appears to me to be at the same time exact and rapid in its execution; moreover, it allows of the exclusive use of volatile reagents. The following is a brief description of it.

I shall suppose that the alloy contains the following elements,—

Silicium,	Iron,
Tin,	Copper,
Zinc,	Lead.

I take about 5 grms. of the substance, and dissolve it in pure nitric acid in a small beaked glass, surmounted by a funnel, which stops the small drops of liquid which are projected; when the solution is effected, the concentrated liquid is boiled for about twenty minutes, then diluted with 2 or 3 times its volume of water, and again boiled for about the same time. These conditions appear to me to be indispensable to give to the oxide of tin and the small quantity of silica all the insolubility of which these substances are capable in nitric acid. The insoluble portion is separated by filtration or decantation, and weighed after calcination; the oxide of tin sometimes has a rose colour, from the presence of traces of gold, which however may be entirely neglected. The mixture, when treated with hydrogen and taken up by muriatic acid, leaves the silica, the weight of which furnishes at the same time the exact amount of oxide of tin.

The nitric liquid, deprived of the tin and silica, is evaporated in a small platinum or porcelain capsule, and the residue is calcined at a dull red heat. In this manner a mixture of the remaining oxides is obtained, in a quantity sufficient to serve for at least two analyses. It need not be weighed, and a few projections during the evaporation do not in any way impair the success of the analysis.

These oxides are triturated in a small glass mortar, and about 2 grms. are put into a small platinum or porcelain tray, and introduced into a small glass tube, about 15 centimetres in length and as narrow as possible, terminated at one extremity by a capillary tube and closed at the opposite end by a cork, which is only used whilst weighing. The tray, the tube, and the cork are weighed together, and the weight of the oxides is determined after they have been heated to a dull red heat in the apparatus, in which a current of dry air is made to circulate. After weighing, hydrogen is substituted for the current of air, and heat is applied by means of a common spirit-lamp until there is no longer any loss of weight. The residue consists of unreduced oxide of zinc, with the copper, iron, and lead in the metallic state. The colour of the mixture will guide the operator, and indicate the conclusion of the experiment. The apparatus is then weighed again, and the loss of weight indicates with great exactness the amount of oxygen contained in the oxides of the three last metals. If the iron and lead be present in negligible quantities, the quantity of copper contained in the alloy may be obtained almost exactly by multiplying the loss of weight by 5, and this gives the composition of the alloy itself. In an approximative analysis of brass, the operation would then be terminated.

A liquid is prepared with sulphuric acid, distilled over sulphate of ammonia, and a quantity of this is poured into 200 or 300 cub. centims. of water, sufficient to dissolve twice the weight of the iron and zinc which may be supposed to be contained in the alloy. The acid liquid is boiled to expel the air completely, and then left to cool in a bottle, which it should nearly fill, and which is closed with a cork, or a small hood of india-rubber, which is particularly adapted for covering beaked glasses. The tray containing the oxide of zinc

and the reduced metals is then put in, when the oxide of zinc and the iron are soon dissolved, the action of the acid upon the latter being facilitated by the presence of the metallic copper. The copper and lead remain, and the vessel is frequently shaken to suspend these metals in the liquid. The whole is left to settle for some hours, then decanted with care, and the residue is washed with boiled water. During this operation a trace of copper or lead may pass, either in the state of sulphate from contact with the air, or conveyed mechanically. This is ascertained by adding to the clear solution a few drops of a limpid solution of sulphuretted hydrogen, and heating it. If a few brown flakes weighing a few milligrammes are deposited, they are separated by decantation, filtered, and added to the metals.

The solution, which contains only sulphates of zinc and iron, is evaporated, the sulphates calcined at about 752° F., and weighed. The weight of the zinc will be calculated at once if there be no iron; this mode of determining zinc is perfect. To separate the iron from the zinc, the sulphates are calcined in a muffle to reduce them to the state of oxides. These are weighed, and moistened with concentrated nitric acid until the zinc is completely dissolved; it is then evaporated to dryness, and heated gently on the sand-bath until the disappearance of the vapours of nitric acid; the nitrate of iron is then decomposed. The mixture is then treated with nitrate of ammonia and a few drops of ammonia, which only take up the zinc; this is decanted, when the weight of the residue of oxide of iron shows the quantity of oxide of zinc in the mixture of oxides. The nitrates of zinc and ammonia might also be evaporated, and the ammoniacal salt driven off by heat, so as to weigh the oxide of zinc directly; but this operation is useless.

The mixture of lead and copper, to which the traces of sulphuret sometimes obtained from the solution of the sulphates of iron and zinc must be added, is dissolved in sulphuric acid mixed with nitric acid; the solution, which is rendered more or less turbid by sulphate of lead, is evaporated to dryness in the sand-bath, and calcined at about 752° F. The mixture of sulphates is weighed, the sulphate of copper separated by means of water, and sulphate of lead is left, the weight of which deducted from the total weight of the sulphates gives the sulphate of copper. The sulphate of copper might also be evaporated and converted into protosulphuret by an excess of sulphur, according to M. Rivot's process; but I have never found any difficulty in determining copper in the form of sulphate by operating with certain precautions, so as not to decompose it. The least heat is sufficient to drive out the excess of sulphuric acid which it might retain. It should be perfectly white at the time of weighing. In case of doubt as to the insolubility of sulphate of lead, the solution of sulphate of copper may be examined for any traces of lead that may have been carried there by washing.

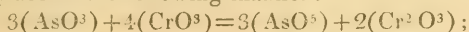
After finding by calculation the weight of each of the simple bodies which enter into the composition of the alloy, the numbers obtained for the silicium and tin are divided by the weight of alloy

acted upon by nitric acid; in this manner the proportion of these bodies contained in 100 parts of the alloy is ascertained. If A be the sum of the proportions of silicium and tin, B the sum of the weights of the other metals calculated from the oxides or sulphates which have served for the determination, in order to obtain the proportion of each of them in hundredths, we have only to multiply the weight of each metal successively by the fraction $\frac{100-A}{B}$. The total must necessarily be =100.

To verify the analysis, the sum of the weights of the oxides obtained directly, or calculated from the sulphates, should be equal to the weight of the oxides put into the tray.—*Ann. de Chim. et de Phys.*, April 1855, xliii. p. 473.

On the Determination of Arsenic. By Dr. H. VOHL.

If arsenious acid be brought in contact with chromic acid in the presence of free sulphuric acid, the former is converted into arsenic acid at the expense of the oxygen of the chromic acid. The oxidation takes place in the following manner:—



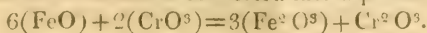
or 297 parts of arsenious acid, containing 225 of arsenic, require for their oxidation to arsenic acid 203·228 of chromic acid, which are contained in 297·516 of bichromate of potash.

But 297·516 of bichromate of potash, brought into contact with oxalate of soda and sulphuric acid, would evolve 264 of carbonic acid, so that 297 of arsenious acid, representing 225 of arsenic, will give rise to a loss of 264 of carbonic acid. From this it is clear that the arsenic may be determined from the quantity of chromic acid reduced. When arsenious acid alone is present, the process consists simply in mixing the substance with a weighed excess of bichromate of potash in the presence of free sulphuric acid and oxalate of soda, and determining the excess of chromic acid from the carbonic acid evolved. If the substance under examination contains the arsenic as arsenic acid, the latter must be reduced by treatment with sulphurous acid; and if both arsenious and arsenic acids occur together, the arsenious acid must be determined in one portion, and afterwards the whole amount of arsenic in another, in which the arsenic acid has been reduced; the amount of arsenic acid is then calculated from the difference. When chlorine is present, oxide of mercury must be added.—*Liebig's Annalen*, May 1855, vol. xciv. p. 219.

On the Quantitative Determination of Iron.

By Dr. H. VOHL.

It is well known that when bichromate of potash and a protosalt of iron are mixed together, the chromic acid is reduced to oxide of chrome, whilst the iron salt is converted into a persalt:—



For the determination of the iron in a protosalt of that metal, it is to be mixed with a weighed excess of bichromate of potash, acidulated with sulphuric acid, and heated to boiling. It is then neutralized with ammonia, and oxalate of soda and sulphuric acid are added to it, so as to determine the excess of chromic acid by carbonic acid. When chlorine is present, oxide of mercury must always be added. As 1 equiv. of bichromate of potash evolves 6 equivs. of carbonic acid, the amount of carbonic acid which the whole of the bichromate of potash should have evolved had no reduction taken place, can easily be calculated; and by deducting from this the quantity actually obtained, the amount of chromic acid employed in the oxidation of the iron is arrived at, and from this the iron is calculated. 168.2 of iron require for their conversion from protoxide to peroxide, 148.7 of bichromate of potash, which corresponds to the evolution of 132 of carbonic acid. If the iron be present in the state of peroxide, it is reduced to protoxide by means of zinc or sulphurous acid; and when it occurs in both states of oxidation, the protoxide is first determined, then the whole amount of iron by a second operation, and the amount of peroxide is calculated from the difference.—Liebig's *Annalen*, May 1855, vol. xciv. p. 218.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Hydraulic Limes, Artificial Stones, and various new applications of the soluble Alkaline Silicates. By F. KUHLMANN.

Theory of Hydraulic Limes.—The author commences by observing, that all limes, and especially hydraulic limes and natural cements, contain considerable quantities of potash and soda. In a memoir read before the Academy of Sciences on the 4th of May, 1841, he considered that these alkalies served to transfer silica to the lime, so as to form silicates, which, when in contact with water, solidify a part of this body by a process of hydratation analogous to that of plaster. In support of this theory, he instances the immediate transformation of common lime into hydraulic lime by simple contact with a solution of silicate of potash. If, during the burning of a limestone, potash is in contact with silica, the silicate formed must necessarily react, if only at the moment when the burnt lime is brought in contact with water.

Further experiments have proved, that by mixing common lime with an alkaline silicate, both finely powdered, in the proportion of 10 or 12 parts of the latter to 100 of the former, a lime is obtained presenting all the properties of an hydraulic lime. If the materials were not well pulverized, the reaction would be incomplete, and an effect subsequent to the solidification would soon cause a disintegration. Thus an hydraulic lime of which the strength may be varied at will, may be immediately prepared with lime and a silicate; and

this will allow of the economical formation of hydraulic constructions in places where there is no hydraulic lime.

Silicatization: Artificial Stones.—From this the author was led to examine the action of the alkaline silicates upon calcareous stones; and the result of his experiments leads him to expect that in this direction the alkaline silicates may be extensively applied to purposes of utility. By suspending powdered chalk in a solution of silicate of potash, a cement is obtained which hardens slowly in the air, acquiring sufficient hardness to be capable of application under certain circumstances in the restoration of monuments, the manufacture of mouldings, &c.

Chalk, either in the natural state or in the form of an artificial paste, when immersed in a solution of silicate of potash, absorbs a certain quantity of silica even in the cold; and this may become considerable by exposing the stone several times alternately to the action of the siliceous solution and to the air. The chalk acquires a smooth appearance, a close grain, and a colour more or less yellowish, according as it is more or less ferruginous. Stone thus prepared is susceptible of a fine polish; and the hardening, which at first is superficial, penetrates by degrees to the centre, even when the stone is of considerable thickness. The process may be employed in formation even of very delicate sculptured ornaments, for when the chalk is very dry, which is essential for the production of good results, the surface undergoes no alteration during silicatization. Thus ornaments of great hardness and unalterable by moisture may be obtained at very small cost, and merely washing ancient monuments formed of soft limestones with a solution of silicate of potash, will preserve them from further decay; the same process may have a still more general application in countries, like Champagne, where chalk is almost the only building material. Since 1841, when these views were first put forward, they have been adopted in practice to a considerable extent.

In the hardening of the siliceous limestones, the carbonic acid of the air appears to separate a part of the silica; and the portions which are in contact with a sufficient quantity of carbonate of lime, pass to the state of silicate of lime.

The author's memoir of 1841 indicated many industrial applications of the artificial injection of mineral substances into the interior of porous bodies, whether organic or inorganic. In the present paper he gives a new series of observations.

The silicatization of sculptures and buildings gives rise to colorations of the stone, which are often very considerable, and render the joints and veins more distinct. In getting rid of this inconvenience, two essential points are to be fulfilled,—chalk walls remain too white, whilst certain ferruginous limestones acquire dark tints. The silicatization of white limestones is effected with a double silicate of potash and manganese. This is a vitreous substance of a deep violet colour, which furnishes a brown solution, and this applied in silicatization, deposits a little oxide of manganese in the artificial siliceous paste. Oxide of cobalt also combines, but in smaller quan-

tity, with the silicate of potash; the silica precipitated by a current of carbonic acid is of a fine azure-blue, and this silicate may be employed in the treatment of white marbles. When the stones are too dark, which is the most general case, excellent results may be obtained by suspending in the solution of silicate, small quantities of artificial sulphate of baryta, which, penetrating into the porous stone, at the same time with the formation of the siliceous layer, remains there, entering into a state of chemical combination. The joinings may be made with ordinary cements, lightened in colour with white substances; but they may be more completely concealed by fragments of the stone itself, mixed with the vitreous silicate of potash, the whole very finely pulverized, and applied in the form of a liquid paste.

Colouring of Stone.—Stones may be tinged of various colours by impregnating them with certain metallic salts, and afterwards producing precipitates of coloured compounds. Thus by impregnating stones with salts of lead or copper, and bringing them in contact with sulphuretted hydrogen gas or hydrosulphate of ammonia, gray, black, or brown shades may be obtained at will. Salts of copper and ferrocyanide of potassium give coppery tints, &c. When porous limestones, and other bodies of analogous composition, are boiled in solutions of metallic sulphates with insoluble oxides, an evolution of carbonic acid takes place, accompanied by a fixation, at a considerable depth in the stone, of the metallic oxides, which enter into an intimate combination with the sulphate of lime. When the oxides are coloured, very pure tints are obtained in this manner. With sulphate of iron, rusty tints of greater or less depth are produced, according to the strength of the solutions; with sulphate of copper the stone receives a fine green tint; sulphate of manganese gives a brown, and a mixture of the sulphates of copper and iron a chocolate colour. The author has also experimented with other sulphates, and with mixtures of them. The affinities which cause these reactions are so powerful, that with some sulphates, such as that of copper, the oxides are so completely absorbed, that after boiling with an excess of chalk, no appreciable trace of them is left in the solution. In operating upon mixtures of sulphate of copper and iron or manganese, the oxides of iron and manganese are the first to be precipitated. The sulphates with colourless oxides furnish analogous results, as does also biphosphate of lime.

In most cases, in order to employ tinted stones in building or in the formation of mosaics, it will be advisable to increase their hardness by silicization. The same will apply to shells, white coral, &c., which may be coloured by the same processes, by operating at different pressures.

The double sulphates formed whilst penetrating into the stone, enter into its composition, and increase its hardness to such an extent, that by the employment of certain sulphates, such as that of zinc, silicization is rendered less necessary.—*Comptes Rendus*, June 25, 1855, p. 1335.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Volatile Bases produced by Destructive Distillation of Cinchonine. By C. GREVILLE WILLIAMS, Assistant to Dr. Anderson, University of Glasgow.

THE history of the organic bases has now become as ardent an object of study among chemists as that of the as yet far more numerous group of acids; and it is generally admitted that the information obtained has been no less important and interesting. Of all organic alkaloids, those of opium and the cinchona barks doubtless occupy the first rank, whether we regard their value as remedial agents, or the remarkable facts which have been ascertained connected with their atomic relations, and the influence exerted by the latter upon the theory of the science.

It has long been known, that many of these fixed oxidized alkaloids may, by destructive distillation and analogous processes, be made to yield an entirely different, and no less interesting class, distinguished from the first by their volatility and the absence of oxygen.

None of the bases produced by such decompositions have attracted more attention than chinoline; not that, like aniline, it has yielded any compounds which, from their perfect analogy with those of ammonia, the beauty of their salts, or any peculiarities in their coloured reactions, are interesting *per se*; on the contrary, the highness of its atomic weight and boiling-point, the small tendency of its salts to form well-defined crystals, and the absence of any specialties in its behaviour with reagents, make it entirely dependent on its stöchiometrical relations, and on its supposed intimate connexion with quinine, cinchonine, and strychnine for the interest it possesses. While chemists believed that those alkaloids, minus a certain amount of hydrogen and carbonic acid, yielded chinoline, a very simple relation appeared to exist between them, a simplicity that gave interest to the subject; but when it was announced that the leukoline of coal-tar was identical with chinoline, and still more, that the product of the action of iodide of methyle on leukole, when converted into a hydrated oxide, was isomeric with quinine, if not the same substance, many were found who believed that the artificial production of the cinchona alkaloids would soon become a

common process. But the evidence of the identity of leukole with chinoline was contradictory. Hofmann first asserted, in his 'Researches upon the Bases of Coal Naphtha,' that their behaviour with chromic acid demonstrated their dissimilarity; while subsequently*, Liebig announced, upon the authority of experiments made by Hofmann, that they had been ascertained, by crucial experiments upon perfectly pure substances, to be the same. In the meantime chinoline is found to be produced from other bodies, among which may be mentioned thialdine and trigenic acid.

But if we examine the published analyses of chinoline, great discrepancies appear, so much so that Gerhardt places two formulæ by the side of the analytical results, namely $C^{18}H^7N$ and $C^{20}H^9N$. On looking at the experimental as compared with the theoretical results, it appears that the analyses, if we except Hofmann's, which were made upon the base from coal-naphtha, agree with neither view. Bromeis, in a paper on chinoline, published about ten years since†, gave a formula which is not admissible; and his numbers, recalculated according to the new atomic weight of carbon, do not agree with either of the formulæ given by Gerhardt, the carbon being 2 per cent. too low. The analysis of the bases themselves in the present case is by no means a satisfactory method of establishing their constitution, for when entirely freed from other substances they are extremely incombustible; and when it is considered that the two formulæ only cause a difference of 0.2 per cent. of carbon, it will be seen that the platinum salts afford a far better means of distinguishing them, the addition of C^2H^2 causing a rise of 2 per cent. in the carbon. But even this method could not afford a result, where a mixture of substances was present, unless the salt had been fractionally crystallized, which does not appear to have been done by either of the chemists who have worked on chinoline; Bromeis obtained far too much carbon for the 18, and as much too little for the 20 C base; the same remark applying, though less strongly, to the results of Gerhardt, whose numbers approach, with regard to the carbon, nearer to the formula $C^{18}H^7N$ than $C^{20}H^9N$, although he obtained greatly too much hydrogen for either.

Before I had seen the discordant analyses in the 'Traité de Chimie Organique' of the last-named chemist, I had suspected, upon theoretical grounds, that chinoline was not a homogeneous substance. In the first place, it appeared unlikely that in an operation with so powerful a reagent as caustic potash, acting at an elevated temperature upon so complex an organic molecule as the base alluded to, that only one substance, and that of so high an atomic weight as chinoline, would be found. I had ascertained, by a great number of experiments on nitrogenized substances, both animal and vegetable, that in no case could they be distilled, either alone or with alkalis, without formation of the pyrrole of Runge, and on trying the same experiment with cinchonine, a similar result presented itself; and

* Chem. Gaz., vol. iii. p. 251, 1845; Proc. of Chem. Soc., April 7, 1845.

† Liebig's Annalen, vol. lli. p. 130.

this alone was a strong evidence of the truth of the supposition alluded to. But the chief reason which led me to doubt the homogeneity of chinoline was, that I was unable to obtain it with a constant boiling-point. I will not lay stress upon an idea which often forced itself upon me, namely, that there might be some basic product besides pyrrole, characteristic of the destructive distillation of nitrogenized organic bodies, because I have no decisive proof; but I may mention that there is a most intimate connexion between the volatile bases best known, produced at very high temperatures. For with all the substances as yet examined, such as bones, shale, &c., the complete series of bases homologous with pyridine has been found; and though, in the case of coal-naphtha, only picoline has as yet been detected, I believe I shall shortly be able to prove that other members of that series exist in it. It will be seen that, if these views are correct, indigo and piperine ought to yield more than aniline in the one case, and piperidine in the other, which, in the present state of our knowledge, does not appear to be the case; while, on the other hand, if we study the experimental results yet obtained from coniine, it will scarcely be too much to conclude that it is a mixture. In order to give a decisive answer to the question raised by these facts, it becomes necessary to examine somewhat minutely several of the bases said to be the sole product of the destructive distillation of certain alkaloids and other nitrogenous bodies; and the following may be regarded in the light of a small contribution to the subject.

It being evident that a considerable amount of material would be required, I subjected 100 oz. of cinchonine to destructive distillation with potash, by small portions at a time, in an iron alembic, the products being collected in a well-cooled recipient; but notwithstanding the large scale on which the experiments were carried on, some difficulty was found in procuring enough of certain portions for examination.

There were several phenomena observed during the preparation of the crude chinoline, which are not described in the works to which I have had access; but as these are not immediately connected with the subject under consideration, they need not be further alluded to, except to mention that whatever precautions were taken in the distillation, pyrrole was nevertheless constantly found, and adhered to the crude chinoline with such tenacity, that it required two days' boiling of the acid solution to effect its complete removal.

The base was separated from the simultaneously-produced water by means of caustic potash, which was added in sufficient quantity to prevent any remaining dissolved. After separation by means of a tap-funnel from the dense alkaline solution, it was again digested with sticks of the potash until no more water was removed. The general process for separating these volatile bases from non-basic and other impurities has been so often described, that it becomes unnecessary to dwell upon it further.

On distilling perfectly dry chinoline with a thermometer in the

tubulature of the retort, ebullition was found to begin at about 300° F. (149° * C.), although no distillate could be procured for nearly fifty degrees above that point until after several rectifications, when it was found that fractions could be obtained at every ten degrees from about 300° to 500° F. (183° to 260° C.). It was therefore determined to submit the whole of the chinoline in my possession to a systematic fractionation; and by the use of very small retorts and tolerably perfect condensation, I was enabled to effect ten fractionations even of the smaller portions; and with the distillates of the higher boiling-points, which were larger in quantity than the others, twelve, and in some cases even thirteen, were effected. Altogether this procedure involved, with those afterwards found necessary, at least 200 distillations. By this means fractions were obtained as low as between 310° and 320° F. (154° to 160° C.), and as high as 520° F. (271° C.). When it is considered that the boiling-point of chinoline is 460° F. (238° C.), it will be seen that it was not going too far to conclude that evidence was obtained of the correctness of the suspicion previously mentioned; and it is submitted that the following experiments prove that cinchonine by distillation with potash yields at least seven bases instead of one, as has been generally believed. It might be imagined that they would all be found to consist of homologues of chinoline, but it will be shown that this is not the case, and that two distinct series are present, one homologous with chinoline, and the other isomeric with the aniline series, and identical in composition with the group found by Dr. Anderson in bone-oil†, and afterwards by myself in the naphtha from the bituminous shale of Dorsetshire‡.

Before proceeding to the details of the experiments, it is proper to mention, that although the researches were commenced in London, and afterwards partially carried on in my own laboratory in Glasgow, that on becoming assistant to Dr. Anderson, he not only permitted me to make comparative experiments with his bases, but gave me every possible opportunity of pursuing the investigation. In my first experiments, and before I had any considerable quantity of chinoline at my disposal, I endeavoured to obtain some insight into the nature of the fluid by fractionally crystallizing the platinum salts according to the method described in a paper on the presence of pyridine in the basic portion of the naphtha from the Dorsetshire shale§.

The results, which are given below, were too remarkable not to be carried out more in detail; but the large quantity of platinum required to effect a perfect separation prevented me from availing myself of this method of working, and I was forced to fall back upon the tedious and wasteful process of fractional distillation.

To obtain the platinum salts, a certain quantity of hydrochlorate

* I have inserted the Centigrade degrees (in round numbers), for convenience of those accustomed to that scale.

† Trans. Royal Soc. Edin., vol. xvi. part 4.

‡ Quart. Journ. Chem. Soc., Lond., July 1854.

§ Phil. Mag., September 1854.

of chinoline, freed from pyrrole, by boiling its acid solution for a long time, was evaporated on the water-bath as long as water came off, but it could not be obtained in a perfectly dry state. The mass dissolved immediately in strong alcohol, showing the absence of ammonia. To the solution a slight excess of bichloride of platinum was added, when a voluminous precipitate (*a*) was obtained; the mother-liquor of *a*, on evaporation, gave a crop of crystals, *b*, the fluid from which gave another crop, *c*.

The precipitate *a* was the first examined; it was dissolved in hot water, and on cooling deposited a crop of crystals, which was evidently a mixture, for it consisted of large orange crystals, *a*³, and exceedingly small needles, *a*⁴; *a*³ was capable of being perfectly freed from *a*⁴ by sifting through muslin; the latter was not however absolutely free from small fragments of *a*³, and was therefore further examined, as will be presently seen.

5.295 grs. of *a*³ dried at 212° gave 1.625 gr. of platinum, or 30.69 per cent., a number intermediate between lutidine and collidine.

The mother-liquid of the crops *a*³ and *a*⁴ gave a crystalline deposit, *a*², which had the same crystalline form and appearance as *a*³, but a little more brilliant in colour.

4.955 grs. of *a*² dried at 212° gave 1.520 gr. of platinum, or 30.67 per cent. It will be seen therefore that *a*² and *a*³ agree not only in form but also in composition.

The mother-liquid of *a*³, on evaporation over sulphuric acid, gave another crop, *a*^{2b}, which was therefore the third crop from *a*.

2.245 grs. of *a*^{2b} dried at 212° gave 0.740 gr. of platinum, or 32.96 per cent., which is almost exactly the theoretical per-centage in picoline (32.94).

It has been said that *a*⁴ contained a little of *a*³ intermixed; it was therefore treated with hot water, which separated it into two portions, one less soluble, *a*⁵, and a solution which on cooling deposited a crop of crystals, *a*⁶. The portion of *a*³ which was present was very minute, and remaining in solution, did not effect the results given by *a*⁵ and *a*⁶.

3.205 grs. of *a*⁵ platinum salt gave 1.010 gr. of platinum, or 31.51 per cent. Lutidine contains according to theory 31.51.

3.970 grs. of *a*⁶ platinum salt gave 1.150 gr. of platinum, or 28.96 per cent., a number intermediate between chinoline and lepidine, presently to be mentioned. The mother-liquid, on treatment in the manner described in my former paper, namely, exposure to a desiccating surface, gave a crop, *a*⁷, of which 2.780 grs. of platinum salt gave 0.880 gr. of platinum, or 31.65 per cent.

The mother-liquor of *a* gave *b* on evaporation; 5.327 grs. of platinum salt *b* gave 1.635 gr. of platinum, or 30.70 per cent., being almost exactly the same result as *a*² and *a*³.

The mother-liquor of *b* gave a crop of white needles, the nature of which I have not yet been able perfectly to comprehend. I have however observed them to exist in the very last crops of many platinum salts of different kinds, more especially when evaporated by

the aid of heat. They are soluble in hot water, and at a red heat leave metallic platinum. They do not deflagrate when thrown into melted nitre. Solution of potash does not decompose them; the aqueous solution is not precipitated by alcohol; the solution in boiling water precipitates nitrate of silver.

2.182 grs. gave on ignition 1.672 gr. of platinum, or 73.50 per cent.

When it is considered that even protochloride of platinum requires 76.6, it will be seen that this experiment does not throw much light on their nature*. The quantity I have as yet been able to obtain has been too small to allow of a further development of their history.

The mother-liquid of these crystals yielded a resin not further examined, which was the last product of the mother-liquid of *a*.

These results, although the numbers obtained are as close as could be expected to the theoretical values, and prove that the bases to be described more fully further on, were not *produced* during the distillations, were of course quite insufficient to settle the points sought to be determined; it became necessary therefore to examine minutely each of the fractions obtained by the distillations previously alluded to. It may be mentioned here, that in order to remove any objections that might be urged as to the bases being produced from the decomposition of nitrogenous impurities existing in the cinchonine employed, an analysis was made with the following results:—

	I.	II.	Calculated.		
Carbon	77.34	..	40 =	240	77.92
Hydrogen	8.09	7.80	24	24	7.79
Nitrogen	..	..	2	28	9.09
Oxygen	..	..	2	16	5.13

The fact of the two series of bases present not being homologous with each other, rendered a considerable amount of labour necessary before they could be purified sufficiently for analysis, the presence in very small quantity of a base of the one series altering to such an extent the composition of the other, that no confidence could be placed in an analysis unless extreme care was taken in the purifications; and the small amount of material at my command naturally added considerably to the difficulties with which I had to contend.

Lutidine.—It soon became evident that the third base discovered by Dr. Anderson in the animal oil of Dippel, and to which he gave the name of lutidine, was that which most prominently presented itself in the first fractions. It was subsequently ascertained that pyridine and picoline were present in exceedingly small quantities, and to attempt their isolation would have been useless. The only evidence I have to show of the presence of pyridine is an isolated result, being the composition of the second crop of crystals of platinum salt obtained from the first fraction during the earlier rectifications, and before the pyridine could have escaped, as being pre-

* It was probably a salt analogous to the bases of Reiset or Gros, mixed with some impurity.

sent in such small quantity it was sure to do eventually, from the difficulty of effecting perfect condensation in an operation involving the changing of the receiver every few minutes.

2·740 grs. of platinum salt, second crop, from fraction boiling below 330° F. (165° C.) (fourth distillation), gave 0·948 gr. of platinum, or 34·6 per cent.. Pyridine requires 34·6.

The difficulty experienced in obtaining the lutidine sufficiently free from the bases above it, to enable a good result to be obtained, will appear from the analyses below, which were made upon platinum salts from fractions which had been rectified the number of times prefixed to each result:—

	1st rect.	2nd rect.	4th rect.	
Carbon	29·40	28·89	27·10	27·20
Hydrogen	3·73	3·84	3·30	3·28
Platinum	30·85	30·63	30·83	

It was evident, therefore, that although the numbers were gradually becoming nearer to those required for lutidine, that nevertheless many more rectifications would be necessary before any close approximation could be expected. The small quantity of fluid was therefore, with careful management, made to pass through nine perfect fractionations, at the end of which a base was obtained, if not absolutely free from the more highly carburetted bases, at least so nearly that on analysis 5·265 grs. of base, boiling between 320° and 330° F. (160° to 165° C.), gave 15·190 grs. of carbonic acid and 4·040 grs. of water, or per cent.,—

Carbon	78·68	14 =	84	78·50
Hydrogen	8·52	9	9	8·41
Nitrogen	12·80	1	14	13·09

This then is the third occasion in which lutidine has been observed, the other two being, first, in bone-oil, where it was discovered*; and secondly, among the bases produced by destructive distillation of the bituminous shale of Dorsetshire, where I found it among others of the same series†.

The analysis of the base from those sources yielded the numbers following, where they are compared with the same base from cinchonine:—

	Dr. Anderson, from bone-oil, mean.	Grev. Williams, from shale naphtha, mean.	Grev. Williams, from cinchonine.
Carbon	78·45	78·68	78·68
Hydrogen	8·81	8·55	8·52
Nitrogen	12·54	12·77	12·80

Before converting the fraction which gave the analysis mentioned above into platinum salt, in order to confirm the result, it was once more distilled, that portion only being received which came over between the same points; the double salt then obtained gave numbers corresponding to, —

* Trans. Royal Soc. Edin., vol. xx. part 2.

† Quart. Journ. Chem. Soc., Lond., 1851.

Carbon	26.94	14 =	84	26.81
Hydrogen	3.36	10	10	3.19
Nitrogen.....	..	1	14	4.49
Chlorine.....	..	3	106.5	34.00
Platinum.....	31.14	1	98.7	31.51

The following analyses of the platinum salts of lutidine relate to the mean results of Dr. Anderson from Dippel's oil, and to a salt obtained by me from shale naphtha; the latter contained however a little picoline, which lowered the carbon:—

	Dr. Anderson, from Dippel.	Grev. Williams, from shale naphtha.
Carbon	26.35	26.14
Hydrogen	3.23	3.16
Platinum.....	31.50	31.76

Although the results detailed leave no doubt as to the identity of this base, it was nevertheless determined to place the fact beyond dispute, by obtaining a methyle compound. When the base is mixed with twice its bulk of iodide of methyle, it becomes heated, boils, and almost immediately solidifies into a mass of crystals of hydriodate of methyl-lutidine-ammonium. This substance, as obtained from the chinoline bases, is excessively soluble in water and alcohol, but insoluble, or nearly so, in æther. On evaporating the spirituous solution of the hydriodate to a syrupy consistence, it retains that state for a considerable time if not disturbed; but immediately it is touched, long and beautiful needles shoot quite across the vessel, and finally the whole becomes a mass of crystals.

As some difficulty presented itself in purifying the crystals from a brown product which contaminates it, in common with analogous salts from almost all volatile oily bases subjected to the same treatment, it was converted into a platinum salt. To effect this the crystals were dissolved in water, the iodine precipitated by nitrate of silver, excess of hydrochloric acid was then added, and the solution filtered; the filtrate, after addition of chloride of platinum, yielded a crop of fine crystals.

4.490 grs. of platinum salt of methyl-lutidine gave 1.360 gr. of platinum=30.29. Theory requires 30.16.

On treating the iodide of methyl-lutidine with potash, no odour of a volatile base is evolved, showing it to agree in constitution with Hofmann's fourth class, and serving also as corroborative evidence of the identity of it with the bone-oil alkaloid.

Collidine.—It now became desirable to ascertain if the next base of the picoline series was present, and the following experiments leave no doubt that collidine exists among the products of the distillation of cinchonine with potash.

Collidine is one of the bases discovered by Dr. Anderson in Dippel's oil*, and found a few weeks subsequently by me in shale naphtha. At the time I examined the latter, I was unacquainted with Dr. Anderson's experiments; but when I became his assistant,

* Trans. Royal Soc. Edin., vol. xxi. part 1.

abundant opportunities were afforded me of comparing the bases I had obtained from both sources with the originals discovered by him, and the result is, that no doubt remains in my mind of their identity, and I have the satisfaction of knowing that Dr. Anderson is of the same opinion.

The quantity of collidine in the crude chinoline, from 100 oz. of cinchonine, was found to be so small that it became impossible to analyse the base itself; the platinum salt however was obtained nearly in a state of purity.

The boiling-point of collidine is stated, in the paper before adverted to, to be 354° F. (179° C.); and on converting the fraction between 350° and 360° F. (177° to 182° C.) of the tenth rectification into platinum salt, the following numbers were obtained:—

	I. and II.	III.			
Carbon.....	29.04	..	16 =	96	29.33
Hydrogen	3.54	..	12	12	3.66
Nitrogen	..	..	1	14	4.31
Chlorine	..	..	3	106.5	32.54
Platinum	29.97	30.2	1	98.7	30.16

Collidine was found to exist also in fractions boiling at higher points; for the next fraction to that last analysed gave a salt which yielded, in a platinum determination, the annexed numbers:—

7.095 grs. of platinochloride of collidine, from fraction boiling between 360° and 370° F. (182° to 187° C.), tenth rectification, gave 2.145 grs. of platinum, or 30.23 per cent.

One cause of the difficulty of obtaining the Dippel's oil series from cinchonine in a state of purity, was the presence of some basic substance decomposable by nitric acid of moderate strength. It was only towards the end of the investigation that this was ascertained. If it had been known at the outset, many of the distillations, and consequently much loss of material, might in all probability have been saved.

The fraction boiling even as high as 390° F. (199° C.) contained a large proportion of collidine; but it was necessary to act upon it with rather weak nitric acid, and then reobtain the base by distillation with potash before converting it into platinum salt. After proceeding in this manner, a fine crop of crystals was obtained, which on combustion with chromate of lead gave numbers corresponding to,—

Carbon	29.56	16 =	96	29.33
Hydrogen	3.56	12	12	3.66
Nitrogen.....	..	1	14	4.31
Chlorine.....	..	3	106.5	32.54
Platinum.....	29.84	1	98.7	30.16

The collidine thus obtained, treated in the usual manner with iodide of methyle, yields a finely crystallized hydriodate of the ammonium base, although the reaction is less energetic than in the case of lutidine.

[To be continued.]

On the Occurrence of Asparagine in the Root of the Rose Acacia
(*Robinia Pseudacacia*). By Prof. H. HLASIWETZ.

When extracted with water, the root of *Robinia Pseudacacia* furnishes a decoction, in which, when it is evaporated to the consistence of a thin syrup, a considerable quantity of hard, rather large octahedral crystals are formed after a few days' standing. These, after being twice recrystallized, are perfectly colourless and strongly refractive; they do not effloresce, grate between the teeth, and have a slightly sweet mawkish taste. Their solution has a neutral reaction, and evolves ammonia when heated with solution of potash; it is not precipitated by acetate of silver or lead, but basic acetate of lead and protonitrate of mercury furnish white precipitates. When heated, the crystals fuse, the mass afterwards becomes brown, swells up, and evolves an unpleasant ammoniacal odour. Finally, they burn without residue. Sulphuric and nitric acids dissolve them without change.

This body is asparagine, as proved by the following analysis:—

C	36.32	8 = 48	36.36
H	6.21	8	6.06
N	..	2 28	21.21
O	..	6 48	36.37

Asparagine appears to occur very commonly in the family of the Leguminosæ, as it has also been found in peas, beans, vetches, liquorice, &c.

The finest preparation is obtained from this root by mere decoction, evaporation, and recrystallizing twice. About 30 lbs. of fresh root furnished more than $2\frac{1}{2}$ oz. of pure substance. This root is therefore to be particularly recommended for the preparation of asparagine.—*Sitzungsber. der Akad. der Wiss. zu Wien, Math. Naturw. Classe*, xiii. p. 526.

On a peculiar Modification of Fibrine.

By E. VON GORUP-BESANEZ.

The author has obtained a form of fibrine from the fluid taken from the cavity of the breast of a tubercular patient, which in its behaviour approaches most closely to syntonine or muscular fibre. It was examined in his laboratory by G. Martius.

Soon after its removal the bloody fluid set into a white trembling mass, which however acquired the usual consistence of such transudations in the course of a few hours. The specific gravity was 1.007. The fibrine collected from this fluid upon linen was treated in the usual way to purify it; it was obtained of a gray colour, and of the tough consistence of blood-fibrine. This condition however underwent a remarkable change when the mass was further washed under cold water; it was converted into a swelled, colourless, transparent, trembling jelly, which was diffused to such an extent in a large quantity of water as to form a homogeneous turbid fluid. This fluid was boiled and filtered whilst hot. A milk-white precipi-

tate remained on the filter, which, dried into thin transparent membranes, under the microscope bore the closest resemblance to flakes of fibrine. Muriatic acid (containing one-tenth) dissolved this mass completely with the aid of a gentle heat. From this solution carbonate of ammonia threw down a white flocculent precipitate.

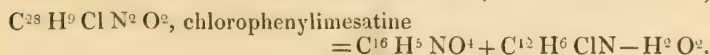
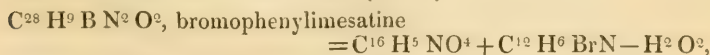
Lime-water does not dissolve the substance even when heated. Dilute solution of caustic potash in the cold produced a gelatinous transparent swelling of the whole mass. Concentrated solution of potash effects its partial solution. The alkaline filtrate, when diluted with water, gave,—

An abundant, whitish, flocculent precipitate with sulphate of magnesia in the cold; with dilute nitric acid, a slight, whitish, flocculent precipitate, and a similar precipitate with acetic acid, added until the neutralization of the alkali. The substance did not dissolve even after long digestion in solution of nitrate of potash (6 parts of salt to 100 of water). When heated on platinum foil, it puffed up, took fire, and burnt with the odour of the albuminates, leaving a bulky cinder, after the complete combustion of which there was a small grayish-white, ashy residue. These reactions therefore agree to a certain extent with those of muscular fibrine; but the partial solubility in caustic, and even concentrated alkalies, and the insolubility in lime-water, distinguish it.—Liebig's *Annalen*, xciv. p. 166.

On the Action of Bromaniline and Chloraniline upon Isatine.

By A. ENGELHARDT.

In a recent paper*, the author has described some compounds which he calls phenylobromimesatine and phenylochlorimesatine; he has obtained similar compounds by the action of chloraniline and bromaniline upon isatine. These bodies, which the author calls chlorophenylymesatine and bromophenylymesatine, in order to distinguish them from the former, are conjugate compounds of chloraniline and bromaniline minus water (H^2O^2):—



Bromophenylymesatine is isomeric with phenylobromimesatine, and chlorophenylymesatine with phenylochlorimesatine. In one series, however, the chlorine and bromine displace the hydrogen in the residuum of the aniline, in the other in the residuum of the isatine.

Bromophenylymesatine, $C^{28}H^9BrN^2O^2$, was obtained by dissolving 3.151 grms. of isatine in a small quantity of boiling ordinary alcohol of spec. grav. 0.863, then adding 3.685 of bromaniline and boiling

* Chem. Gaz., No. 305, July 2, 1855, p. 241.

for some time. The fluid sets, on cooling, into a mass of fine orange-yellow needles. These were purified by washing with weak alcohol, and recrystallization from strong alcohol. 3.151 grms. of isatine and 3.685 grms. of bromaniline gave 5.683 grms. of bromophenylimesatine.

Properties.—It crystallizes from alcohol in fine, flexible, silky, orange-yellow needles. When heated on platinum foil, it fuses, and is then decomposed, leaving a coal. It is almost insoluble in water, but dissolves readily in boiling alcohol; cold alcohol dissolves much less of it. It dissolves in strong muriatic acid when heated and is decomposed thereby, furnishing a red solution, from which small red crystals of isatine are deposited on cooling, whilst the decanted mother-liquor, when diluted with water and mixed with caustic potash, furnishes a white precipitate of bromaniline. The alcoholic solution of bromophenylimesatine, when boiled with muriatic acid, is decomposed into isatine and muriate of bromaniline. When heated with an aqueous solution of caustic potash, bromophenylimesatine at first acquires a red colour, and afterwards dissolves; bromaniline is then separated, and a yellow solution is formed, which becomes red on the addition of muriatic acid, and deposits isatine. Analysis:—

C		56.45	28 =	168	55.81
H		3.50	9	9	2.99
Br		..	1	80	26.58
N		..	2	28	9.30
O		..	2	16	5.32

Chlorophenylimesatine, $C^{28}H^9ClN^2O^2$.—Prepared in the same way as the preceding compound, but with 2.325 grms. of isatine and 2.012 grms. of chloraniline; it crystallizes from alcohol in orange-yellow capillary needles. It is insoluble in water, but dissolves readily in boiling, and more sparingly in cold alcohol. Its behaviour with the above-mentioned reagents corresponds exactly with that of bromophenylimesatine. Analysis:—

C		66.05	28 =	168.0	65.50
H		3.73	9	9.0	3.51
Cl		..	1	35.5	13.84
N		..	2	28.0	10.91
O		..	2	16.0	6.24

Nitrophenylobenzamide, $C^{26}H^{10}N^2O^6 = C^{14}H^5O^3, C^{12}(H^4NO^4)HN$.—Chlorobenzoyl acts upon chloraniline and nitraniline in the same way as upon aniline. 0.58 grm. of the acicular crystals of nitraniline, treated with chlorobenzoyl, acquired a white colour, but otherwise exhibited no change in their appearance. When heated subsequently they all dissolved, and the solution afterwards formed a hard crystalline mass. This mass was treated with water and a solution of carbonate of soda; the residue was dissolved in boiling alcohol, and left to crystallize. By recrystallization the body is obtained in nacreous scales. Analysis:—

C	64.68	26 =	156	64.46
H	4.36	10	10	4.13
N	..	2	28	11.57
O	..	6	48	19.84

Chlorophenylobenzamide, $C^{26} (H^{10} Cl) NO^2 = (C^{14} H^5 O^2) (C^{12} H^4 Cl) HN$, was obtained by treating chloraniline with chlorobenzoyl. Muriatic acid is evolved. The body crystallizes in transparent hexagonal tables, which are decomposed with difficulty when heated with fused caustic potash, setting chloraniline free.—*Bull. de St. Pétersb., Cl. Phys. Math.*, xiii. p. 379.

Tannic Acid a Remedy for Chilblains. By Prof. BERTHOLD.

The extract obtained by boiling $1\frac{1}{2}$ oz. of pounded nut-galls with 0.5 lb. of rain-water, has an excellent action upon chilblains. The decoction may be employed as a bath, or laid upon the swellings by means of rags. The itching and burning disappear in two or three days. In old cases the remedy must be continued longer. Oak-bark may also be employed; a mixture of 1 lb. of oak-bark and 2 lbs. of water being applied as a poultice. This remedy must not be used with broken or festering chilblains.—*Göttinger Gel. Anz. Polytechn. Centralblatt*, 1855, p. 704.

ANALYTICAL CHEMISTRY.

On the Quantitative Separation of Oxide of Iron from Alumina.
By Dr. I. WEEREN.

THE author recently published a method for the *indirect* separation of alumina from the oxides of iron; but as *direct* methods are always to be preferred to indirect, he has continued his researches, and in the present paper gives a process for the direct determination of these substances.

It is well known that the behaviour of all the *weaker* inorganic bases towards most reagents undergoes a change in the presence of many organic substances, such as tartaric acid for instance; the hydrosulphates however especially make an exception to this rule. It is also well known that the metals which can only be precipitated from alkaline compounds by sulphuretted hydrogen, are thrown down by sulphuret of ammonium as sulphurets; whilst, on the other hand, those earths which, unlike the magnesia group, do not form readily soluble double salts with the ammoniacal salts, are only thrown down as hydrates by the above reagent.

The former of these circumstances is the origin of the defects presented by the previous methods for the separation of alumina and oxide of iron; but the author's method for the direct separation

of these substances is founded upon both of them, so that it does not partake of these defects.

If a solution containing oxide of iron and alumina be mixed with a sufficient quantity of tartaric acid, the separation of the bases by ammonia is completely prevented. But if it be supersaturated with ammonia and then mixed with sulphuret of ammonium, the whole of the iron is separated as sulphuret of iron, whilst the whole of the alumina remains in solution. The separation of sulphuret of iron in the presence of organic substances is attended with some difficulty, but the author has got over this in the following manner.

The operations are carried on in a flask, which can be closed by a ground stopper. After supersaturation with sulphuret of ammonium, the flask is filled within a few cubic centimetres with hot water, well shaken, and left to stand in a warm place. When the whole of the sulphuret of iron has subsided, and the supernatant fluid has acquired a yellow colour, the glass stopper is carefully taken out, without disturbing the precipitate, and replaced by a cork bored with two holes. In one of these a siphon-tube is placed, so that it may be raised and lowered without admission of air; it is so arranged that its shorter leg, which enters the flask, may be about 4 to 6 millims. above the precipitate of sulphuret of iron. The other opening receives a tube bent at right angles, by means of which the apparatus may be united with a constant sulphuretted hydrogen apparatus. When this gas is passed slowly into the flask, the supernatant fluid flows off through the siphon; it is stopped by turning off the stop-cock of the sulphuretted hydrogen apparatus when the fluid has nearly reached the bottom of the siphon. The flask is then inclined in such a manner that the longer limb of the siphon may be higher than the shorter one, when, on loosing the cork or stopping the connexion with the sulphuretted hydrogen apparatus, the fluid contained in the siphon runs back into the flask. The shorter leg of the siphon is then cleaned if necessary, and the flask, which is afterwards filled as above with warm water containing sulphuret of ammonium, closed with the glass stopper, shaken, and left in a warm place until the complete deposition of the precipitate. This washing is repeated several times, and the precipitate is then brought upon a filter, when it is again washed several times with water containing sulphuret of ammonium. It is unnecessary to devote great care to the cleaning of the flask from sulphuret of iron, as the small quantity that remains is quite free from alumina, and may be dissolved in the muriatic acid employed for the decomposition of the sulphuret of iron.

The sulphuret of iron is dissolved in muriatic acid to which a little nitric acid has been added, and the solution of chloride of iron produced is filtered. The iron is separated from the filtrate by ammonia, and the precipitate is afterwards washed, dried, calcined and weighed. When the washing in the flask has been continued so long that there is no doubt of the removal of all the alumina, the precipitate may be decomposed at once in the flask by muriatic acid containing nitric acid.

The washing-water separated from the sulphuret of iron which contains the alumina is evaporated at first over the open fire or in a digester, and afterwards to dryness on the water-bath. The residue is put into a crucible and calcined, the heat being very gradually raised to the highest degree attainable by a Berzelius-lamp. If the amount of charcoal be small, it is to be completely burnt; but if it be considerable, it must be treated with boiling muriatic acid, and the alumina precipitated from the filtered solution by sulphuret of ammonium.

The complete combustion of the carbon may usually be neglected when alumina and oxide of iron have been originally partially dissolved in muriatic acid, and an excess of carbonate of soda has been added in order to avoid the formation of volatile chlorides; care must be taken that the whole of the tartaric acid is carbonized, and for this purpose a continued low temperature is best.

Analytical Proofs.

I. 0·576 grm. of alumina and 0·2475 grm. of oxide of iron in solution in nitric acid, gave 0·5712 grm. of alumina and 0·2473 grm. of oxide of iron.

The loss of alumina was produced by the sudden deflagration of a portion of the carbon with the nitrates during the destruction of the tartaric acid, which projected a small quantity of the substance from the cup.

II. 0·5121 grm. of alumina and 0·5773 grm. of oxide of iron gave 0·5110 grm. of alumina and 0·5756 grm. of oxide of iron.

III. 0·0896 grm. of alumina and 0·5773 grm. of oxide of iron gave 0·900 grm. of alumina and 0·5750 grm. of oxide of iron. Results:—

	I.		II.		III.	
	Calculated.	Found.	Calculated.	Found.	Calculated.	Found
Alumina . . .	67·72	67·16	47·01	46·91	13·42	13·50
Oxide of iron	32·28	32·12	52·99	52·84	86·58	86·23
	100·00	99·28	100·00	99·75	100·00	99·73

Poggendorff's *Annalen*, 1855, xcv. No. 7. p. 397.

On the Separation of Alumina from Oxide of Iron.

By R. RICHTER.

When alumina has to be separated from oxide of iron which is accompanied by manganese, lime and magnesia, the author, instead of extracting the precipitate of oxide of iron and alumina containing lime and magnesia, obtained by ammonia, by boiling it with potash, fuses the precipitate with 10 times the quantity of carbonate of soda, and then, by means of water with the addition of potash, dissolves the alumina as aluminate of soda and potash. The separation in other respects is effected in the ordinary manner, but is more complete.—*Journ. für Prakt. Chem.*, lxiv. p. 370.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Aluminium.

By MM. H. SAINTE-CLAIRE DEVILLE and DUMAS.

M. SAINTE-CLAIRE DEVILLE, in presenting to the Academy of Sciences some specimens of aluminium prepared at the expense of the Emperor of the French, gave the following summary of the mode of preparation of this metal. The principal materials employed in the industrial production of aluminium are chloride of aluminium and sodium.

The chloride of aluminium is obtained by the reaction of chlorine upon a mixture of alumina and coal-tar, previously calcined. The operation is effected in a gas retort with remarkable facility and completeness. The action of the chlorine is complete upon a stratum of the mixture of from 1 to 2 decimetres in thickness, the whole of the gas being absorbed. The condensation of the chloride of aluminium is effected in a chamber lined with glazed brick-work. It is a compact substance, of considerable density, and composed of sulphur-yellow crystals. This chloride contains very little iron, and it is entirely purified during its treatment for aluminium by passing its vapour over iron points heated to about 750° F. The sesquichloride of iron, which is as volatile as the chloride of aluminium, is converted into protochloride by contact with the iron, and becomes comparatively fixed. The vapour of chloride of aluminium on leaving the apparatus furnishes colourless transparent crystals.

The sodium is now prepared in large and small vessels with remarkable facility. The author has carefully studied the influence of temperature, of the surface exposed to heat, and of the issue of the vapour of sodium from his apparatus, and ascertained that by a suitable arrangement of the proportion between the surface exposed to heat and the section of the tubes which give passage to the sodium, this metal may be produced at a low temperature, perhaps near that of the point of fusion of silver. The sodium is already prepared at a lower temperature than that employed in the manufacture of zinc. He is now engaged in the production of sodium by a continuous process.

The reaction of the chloride of aluminium upon the sodium is effected in metallic tubes, of which the form and arrangement are not yet sufficiently adapted for industrial purposes. The author however hopes soon to get over these difficulties by experiments, which are already planned.

At the same meeting, M. Dumas exhibited some large and fine masses of chloride of aluminium, metallic sodium, and aluminium in bars, prepared by M. Sainte-Claire Deville. The manufacture of chloride of aluminium has already been carried to quantities of 200 to 300 kilograms, so that its capability of being effected industrially is no

longer a matter of doubt. M. Deville's process furnishes sodium with surprising facility; and as both the chloride of aluminium and sodium are pure, the aluminium furnished by them is equally so.

The materials employed in the production of 1 kilogram. of aluminium, viz. ammonia-alum, chlorine, charcoal, carbonate of soda and chalk, are all very cheap; and it would not appear surprising that the whole should already be reduced to 32 francs at the outside, if at the commencement of these researches the price of sodium had not been 1000 francs the kilogram., which alone rendered the cost of aluminium 3000 francs.

Thus these investigations have not only shown the possibility of extracting aluminium on a large scale by manufacturing processes, but will also furnish science with a very important reagent, sodium, at a very moderate price. The numerous trials which have been made prove that its extraction is as easy as that of zinc; that it may be exposed to the air when fused without taking fire; and, lastly, that it will flow from the apparatus in which it is made.

It will be also observed that this mode of preparation of aluminium opens a new course in metallurgy. Hitherto metals have been always obtained by the reduction of their oxides with charcoal, but the extraction of aluminium on the large scale shows that metals may be obtained from their chlorides. With some metals this process is indispensable; with others it may be preferable to the old methods.

M. Dumas mentions that aluminium is exceedingly sonorous, equalling in this respect the bronze employed for bell metal, a quality which, as he observes, is not known to exist in any other pure metal. He concludes his remarks by pointing to Marseilles as the most proper locality in France for the manufacture of aluminium, as all the materials required can be obtained there at the most favourable rates, and large quantities of muriatic acid are actually wasted in that city.—*Comptes Rendus*, June 18, 1855, p. 1296.

Analysis of an Enamel for Cast Iron. By A. FAISZT.

In the Technical Dictionary of Karmarsch and Heeren, there are directions for enamelling cast-iron kitchen utensils. This enamel must however cost more than one from Silesia, of which the following is an analysis. I. is white glazing for the enamel; II. a reddish glazing; and III. the ground of the enamel:—

	I.	II.	III.
Silica	47.96	42.46	79.83
Alumina	1.19	6.39	3.39
Lime	11.27	0.73	
Oxide of tin ..	10.68	12.66	
Soda	38.51	37.13	
	99.61	99.37	

Except soda, no other base was present in the ground; the quantity could not be determined from a deficiency of material.—*Gewerbebl. aus Württemberg*, 1855, No. 13.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 21, 1855. (The Lord Wrottesley, President, in the Chair.)

“Contributions to the History of Aniline, Azobenzole and Benzi-dine.” By A. W. Hofmann, Ph.D., F.R.S.

The transformation of nitrobenzole into aniline by the action of sulphuretted hydrogen is attended with such difficulties and requires especially so much time, that chemists hitherto have generally preferred to prepare this base from indigo. Lately a new modification of Zinin's process has been adopted by M. A. Béchamp*, which consists in submitting nitrobenzole to the reducing action of acetate of protoxide of iron. This process—M. Béchamp simply uses a mixture of iron and acetic acid—is applicable to all nitro-compounds, and has been extensively tried with the most perfect success in the laboratory of the Royal College of Chemistry. The facility of the process, its rapidity, and the large amount of product it yields in most cases, cannot fail materially to assist the study of the volatile organic bases.

During these experiments several observations were made, which I beg leave to bring under the notice of the Society.

When employing about double the amount of iron which is recommended by M. Béchamp (2·5 instead of 1·2 of iron to 1 part of nitrobenzole), Mr. Alfred Noble found that the latter portion of the distillate solidified partly in the receiver and partly in the condenser. Washed with hydrochloric acid from adhering aniline, and once or twice recrystallized from boiling alcohol, the solid matter was obtained in fine crystals of a yellowish-red colour, and fusing below the boiling-point of water. These crystals possessed all the properties of azobenzole, which was moreover identified by combustion.

0·260 gramme of substance gave 0·755 grm. of carbonic acid and 0·134 grm. of water.

The well-established formula of azobenzole, $C_{12}H_5N$, requires the following values:—

Theory.			Experiment.
	Equivalents.	Per-centage.	
Carbon	12	79·12	79·12
Hydrogen	5	5·49	5·76
Nitrogen	1	15·39	
100·00			

The azobenzole obtained in this manner is so readily purified that this process is greatly preferable to the action of alcoholic potassa upon nitrobenzole, since the latter process simultaneously produces several substances which can be separated only with difficulty from the azobenzole.

A portion of the azobenzole obtained in the above process was

* Chem. Gaz., March 1, 1855, p. 81.

converted by means of sulphuretted hydrogen into benzidine. Of the beautifully crystallized compound, a platinum salt was made which was analysed by Mr. Noble.

0.268 grm. of the salt left 0.088 grm. = 32.88 per cent. of platinum. The formula $C_{12}H_6N, HCl; Pt Cl_2$ requires 33.09 per cent. of platinum.

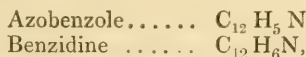
Benzidine exhibits a very interesting deportment with nitrous acid; gently warmed in the gas of this acid, obtained by treatment of starch with nitric acid, it gives rise to a powerful reaction. The substance assumes an orange-red colour, and exhibits, after treatment with water, when recrystallized from alcohol, all the properties of azobenzole.

The reproduction of this body from benzidine was moreover fixed in the following numbers:—

0.215 grm. of substance gave 0.623 grm. of carbonic acid, and 0.112 grm. of water.

	Theory. ($C_{12}H_5N$).	Experiment.
Carbon	79.12	79.02
Hydrogen	5.49	5.78
Nitrogen	15.39	
	100.00	

The simplest formulæ of azobenzole and benzidine only differ by one equivalent of hydrogen,—



a relation which sufficiently explains the transformation and reproduction of azobenzole.

“On the Formation and some of the Properties of Cymidine, the Organic Base of the Cymole Series.” By the Rev. John Barlow, F.R.S., Sec. R. Inst.

The object of this memoir is to detail the process by which an organic base, provisionally named *Cymidine*, was obtained from the hydrocarbon, cymole, and to describe some of its properties, and certain phenomena attending its production.

The substitution-product, nitrocymole, was procured by acting on cymole by strong nitric acid, both liquids being kept at the temperature $-17\frac{7}{9}^{\circ}$ Cent. (0° Fahr.). From nitrocymol, cymidine was obtained by Béchamp's modification of Zinin's process, and results of analyses, made by combustion of the platinum salt, and likewise by a silver determination of the hydrochlorate, were found to coincide with the formula $C_{20}H_{15}N$. In the formation of cymidine a neutral oil occurred, having the same boiling-point with cymole. From this hydrocarbon a substitution compound was derived, apparently isomeric with, but possessing a less specific gravity than nitrocymole. This nitro-compound was also subjected to the process of reduction

already described, and a basic substance was formed from it, which was identified by a platinum determination with cymidine. Some qualitative experiments, made with cymidine, were also described, and the memoir concluded with the following synoptical table of the homologues of the benzole series.

Hydrocarbons.	Nitro-substances.	Bases.
Benzole $C_{12}H_6$	Nitrobenzole $C_{12}H_5NO_4$	Aniline $C_{12}H_7N$
Toluole $C_{14}H_8$	Nitrotoluole $C_{14}H_7NO_4$	Toluidine $C_{14}H_9N$
Xylole $C_{16}H_{10}$	Nitroxylene $C_{16}H_9NO_4$	Xylidine $C_{16}H_{11}N$
Cumole $C_{18}H_{12}$	Nitrocumole $C_{18}H_{11}NO_4$	Cumidine $C_{18}H_{13}N$
Cymole $C_{20}H_{14}$	Nitrocymole $C_{20}H_{13}NO_4$	Cymidine $C_{20}H_{15}N$

Letter from Dr. Herapath to Professor Stokes, "On the Compounds of Iodine and Strychnine."

June 20, 1855.

MY DEAR SIR,—Will you do me the favour to announce to the Royal Society, that I have been engaged, during some months past, in investigating the optical and chemical properties of some crystalline compounds of iodine and strychnine which appear to be strongly indicative and peculiar? One of these bodies, from the analysis hitherto made, would seem to have a formula not very different from the following, viz. $C^{42}H^{22}N^2O^4 + I^5$, and crystallizes in hexagonal prisms, passing by the ordinary replacement planes to the acute rhombohedron and other forms, all apparently derived from the rhombohedral system; some of these crystalline forms are very strange and unusual. This substance possesses "double absorption" in a very evident degree, and when examined by vertically plane polarized light, the hexahedral prisms are all obstructive of the polarized beam when the length of the prisms lies parallel to the plane of the incident ray; in this position they appear dark sienna-brown in colour; when the long axis of the prisms lies perpendicular to the plane of primitive polarization the crystals transmit a lemon-yellow tint, passing through greenish yellow to sherry-brown.

The other substance appears to be the sulphate of iodo-strychnia, and has a decidedly metallic green reflexion, crystallizes in stellate aggregations of prisms, brilliantly green by reflected light, but having a deep blood-colour by transmission; these also possess double absorption and are very peculiar, as a slight increase in thickness renders them wholly impervious to light.

When these matters have been more carefully worked out, I hope to have the pleasure of communicating the results to the Society: in the mean time the present notice will be sufficient for the object in view.

I remain, my dear Sir,

Yours very truly,

W. BIRD HERAPATH.

Professor Stokes, F.R.S.

THE CHEMICAL GAZETTE.

No. CCCIX.—September 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Root of Ononis spinosa. By Prof. H. HLASIWETZ.

Ononine.—Reinsch was the first to mention this body. He gives a prescription for its preparation, which furnishes it mixed with another substance. The author has adopted another method of preparation. The root is boiled for about an hour with water; and the decoction, after it has become somewhat clear by settling, is precipitated with solution of acetate of lead, which is added in slight excess. The precipitate, which is of a dingy light brown colour, is filtered; it contains, together with substances resembling tannic acid and glycyrrhine, a small quantity of citric acid and nitrogenous subordinate constituents. It cannot be further employed with advantage.

The excess of acetate of lead in the filtrate is now got rid of by sulphuretted hydrogen; the sulphuret of lead is collected, washed, and quickly dried by a gentle heat; it is then triturated and extracted three times with strong alcohol. The combined alcoholic fluids are distilled off, and the residue left to crystallize. These fluids are of a more or less brown colour, and first of all deposit a little sulphur in small crystals, which are removed. After standing a short time, rough, warty, yellow masses are obtained; these are crude ononine. They may be freed from the greater part of the brown resinous body by which they are contaminated by means of cold alcohol, which is allowed to drop through them in a displacement funnel.

They are then crystallized four or five times, and decolorized by animal charcoal. Ononine has a tendency to crystallize from alcohol in warts and grains. These are often unrecognizable as crystals by the naked eye, but are seen to be prisms under the microscope. It is difficult in this manner to obtain it quite distinctly crystallized and of a dazzling white colour.

Ononine dissolves even in strong alcohol only after long boiling; in water it is difficult of solution. However, like many other difficultly soluble organic substances, it may be taken up, after long boiling, by water and moderately strong alcohol. When water is poured over it in a retort, and after it has boiled for a few minutes, strong alcohol is gradually added, a very faintly-coloured solution is obtained, and this, on cooling, lets fall the greater part of the body

in flakes, which consist of small perfectly colourless prisms. If it be then crystallized once more, it may be regarded as perfectly pure.

By converting the precipitate produced with acetate of lead into sulphuret of lead, and treating this in the same manner as above, a further small quantity of ononine may be obtained.

This method of preparation does not perhaps furnish the whole of this crystallizable matter that is contained in the root, and more was obtained by a different process from alcoholic extracts of the root; but in this case the substances, although apparently pure, were always very variable in their composition.

The ononine prepared by the author appeared from its behaviour to be identical with that prepared by Trommsdorff by the following process. The dry root was extracted with alcohol, the alcohol distilled away from the tincture obtained, and the residue repeatedly treated with warm water. The portion not dissolved in water was dissolved in alcohol, boiled with litharge, and filtered. The filtrate was distilled down to one-eighth, and the ononine which separated on cooling purified by pressure and recrystallization. The fluids obtained by treating the alcoholic extract with water were also precipitated with solution of acetate of lead, the precipitate treated with sulphuretted hydrogen, the sulphuret of lead dried and repeatedly extracted with alcohol, the tincture evaporated by distillation, and the dried residue purified by crystallization; it appeared to be the same as the preceding.

Properties of Ononine.—It is perfectly colourless, free from nitrogen, and consists of prismatic needles or laminæ. These do not dissolve in cold water, and but very sparingly in boiling water. The boiling solution becomes turbid on cooling; microscopic tufted needles are separated. Æther scarcely dissolves it at all, but boiling alcohol gradually dissolves it entirely. It is inodorous and tasteless. When concentrated sulphuric acid is poured over it, it dissolves with a reddish-yellow colour, which in course of time becomes cherry-red.

If a few crystals be put upon a watch-glass, and sulphuric acid be dropped upon them, a fine carmine-red colour is immediately produced on the addition of a little oxide of manganese; this is characteristic of the body. It is however unstable. The commercial article often gives a violet colour by this treatment; this arises from a product of decomposition, which will be described hereafter.

When heated on platinum-foil, ononine fuses, and afterwards burns with flame. The odour of ononine, when decomposed by heat, is like that of non-nitrogenous bodies in general. The coal burns readily, without residue.

When ononine is floated upon an oil-bath in a small porcelain cup as thin as paper, the temperature of the bath must be raised to 455° F. before the ononine fuses. It becomes brown, and diffuses the odour of decomposing substances before melting. The fused brownish mass solidified in a crystalline form after some time. It had lost 2.65 per cent. in weight, a loss which however cannot be regarded merely as water. The fused mass continued tasteless, and

showed the same degree of solubility as before. The reaction with oxide of manganese and sulphuric acid was also the same. Nitric acid dissolves ononine when boiled, with a dark yellow colour; oxalic acid is formed.

Cold muriatic acid has no apparent action upon ononine. When boiled with it in a test-tube, it dissolves, but the fluid is immediately rendered turbid by microscopic needles united into flakes, which consist of a new body. If it be boiled longer, the fluid becomes somewhat discoloured, and the crystalline precipitate acquires a slight violet colour. The presence of sugar in the filtrate may be detected after saturation with solution of soda. Solution of potash dissolves ononine by boiling; baryta-water effects this still more readily. It is not taken up even by a large quantity of liquid ammonia.

Its alcoholic solution gives no precipitate with metallic salts, except basic acetate of lead, which furnishes white flakes. No essential change of colour is produced by perchloride of iron. Solution of chlorine effects no change in ononine. Analysis gave,—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
C =	58.28	58.54	58.61	59.28	59.78	61.32	60.77	61.75	60.55
H =	5.45	5.51	5.48	5.61	5.52	5.66	5.72	5.68	5.76
O =	35.27	35.95	35.91	35.11	34.70	33.02	33.51	32.75	33.69

The author did not consider it advisable to deduce a formula from these numbers, but endeavoured to obtain this from the products of decomposition. The decomposition best fitted to explain the constitution of ononine is that effected by baryta-water. Under the influence of this reagent ononine is decomposed into an acid, which is obtained in combination with baryta, and a new body, belonging to the series of conjugate hydrates of carbon. The acid is formic acid, the glucosogenous body is a substance hitherto unknown, to which the author gives the name of *onospine*.

When ononine is boiled for a long time in a retort with baryta-water, it dissolves at last entirely. The last portions disappear slowly, and only on the addition of new portions of baryta-water. The fluid is clear and of a pure yellow colour. During the boiling a faint aromatic smell is generally perceived. On cooling, and especially when placed in ice, the fluid becomes turbid, and a small quantity of the new body is thrown down with some carbonate of baryta. Carbonic acid is passed into the fluid until the strong effervescence has entirely ceased; the precipitate is filtered and washed with cold water, then taken whilst moist from the filter, and repeatedly extracted by boiling with water. The hot filtered fluid immediately becomes milky, and when perfectly cooled it sets into a jelly of small scaly crystals, which are individually strongly refractive. After draining upon a filter, they are three or four times recrystallized from water and treated with animal charcoal. The crystals dissolve readily in alcohol, and crystallize from this solution in concentrically-grouped needles. It is advisable to stir the baryta precipitate with a few drops of very dilute sulphuric acid, before ex-

tracting it with hot water, as by this means a baryta compound into which the onospine enters is decomposed.

When the mixed precipitate produced by carbonic acid was filtered off, and the clear fluid had been exposed for a night to a temperature approaching the freezing-point, an amber-yellow deposit of a resinous appearance was formed, which on drying acquired a cracked gum-like aspect. When separated from the fluid, it is readily soluble in alcohol, and consists of baryta and onospine in variable proportions. The alcoholic solution by spontaneous evaporation begins, after standing for some days, to form crystalline points. Sulphuric acid decomposes the alcoholic solution; and the fluid filtered from the BaO , SO^3 again furnishes crystallized onospine. If it is not required to obtain the acid existing combined with baryta in the fluid, it would be just as well to effect the decomposition at first with sulphuric acid instead of carbonic acid. But even a small excess of sulphuric acid is to be avoided, as it decomposes the onospine by boiling.

When the fluid filtered from the baryta precipitate produced by carbonic acid was heated to boiling, a further portion of baryta was thrown down with evolution of carbonic acid; this was dissolved by the excess of carbonic acid. The fluid was then again evaporated in the water-bath. On the cooling of the fluid thus concentrated, a further slight separation of baryta was observed; this must also be removed. When at last the fluid was reduced to a very small volume, so that it had an oily consistence, small granular crystals of formiate of baryta, united in groups, were formed in it after standing for a day or two.

Onospine.—The body obtained in this manner is perfectly white after repeated recrystallization from water, and dries on the filter into a slimy film, consisting of small crystals, which appear tabular under the microscope. They can only be separated from their interlaced state by rubbing with the fingers, by which they are rendered somewhat electrical. They dissolve to any amount in boiling water; the solution is limpid, and sets on cooling into a crystalline jelly. The crystals dissolve readily in alcohol, and they again shoot into radiate prisms in this solution. They are nearly insoluble in æther. Caustic alkalies and ammonia dissolve them readily, and acids precipitate them again. From their solution in ammonia they crystallize again unaltered after the evaporation of the ammonia. When concentrated sulphuric acid is poured upon them in a watch-glass, they dissolve with a reddish-yellow colour; the addition of a few particles of oxide of manganese to the solution changes the colour to a deep carmine-red. The reaction resembles that produced by sulphuric acid upon salicine, but the colour is more intense.

Nitric acid oxidizes the body with formation of oxalic acid. The aqueous solution gives no precipitate with any metallic salts except basic acetate of lead. Nitrate of silver is not reduced by it, even when boiled. When heated upon platinum, onospine melts, and when further heated burns with flame and without residue, producing an odour resembling that of sugar.

When heated in a glass tube, a very small quantity is sublimed. The melting-point is about $323^{\circ}6$ F., but the temperature was raised to 392° F., without any decomposition being perceptible. It solidified in a gum-like form to a cracked mass, and lost nothing in weight. The fused mass becomes very electrical when pounded; it is very hygroscopic, and becomes opaque; and whilst the crystals are nearly tasteless, a bitter astringent taste is observed after fusion. Boiling water again dissolves the fused onospine, and it separates as before in a crystalline form.

Perchloride of iron gives a very sensitive reaction with the aqueous and alcoholic solutions. It is a dark cherry-red colour, which is almost the same as that produced by phloridzine.

Dilute sulphuric acid and muriatic acid decompose onospine when heated. It dissolves first of all, and immediately afterwards crystals are deposited, which attach themselves to the sides of the vessel. The fluid filtered therefrom and neutralized exhibits very distinct reactions of sugar, both according to Trommer's and Pettenkofer's methods. Onospine itself does not reduce an alkaline solution of oxide of copper. Analyses of the substance dried at 212° F. gave,—

I.	II.	III.	IV.	V.	VI.
C = 60.26	60.54	60.03	..	59.72	60.07
H = 6.08	6.01	6.02	5.9	6.13	6.19
O = 33.66	33.45	33.95	..	34.15	33.74

Onospine is one of the so-called glucosogenous substances, a conjugate hydrate of carbon. It is not identical with any of the previously-known bodies of similar constitution. In its behaviour it approaches most nearly on the one hand to salicine, and on the other to phloridzine. By the action of sulphuric or muriatic acid it is readily decomposed into its constituents, to one of which the author gives the name of *ononetine*. The author endeavoured to settle the formula of onospine, as well as that of ononetine, by a quantitative determination of the sugar.

[To be continued.]

On the Volatile Bases produced by Destructive Distillation of Cinchonine. By C. GREVILLE WILLIAMS, Assistant to Dr. Anderson, University of Glasgow.

[Concluded from page 309.]

Chinoline.—In examining the fractions at temperatures above those already described, it appeared that the series which then presented itself was not homologous with that of which lutidine and collidine are members. In fact, about 400° F. (204° C.) the proportion of hydrogen in the platinum salts began to lower so rapidly, that it was evident that the chinoline of Gerhardt was the next base.

In the course of the rectifications, the relative positions of the bases undergo considerable changes, for while in the eighth rectification the portion of fluid boiling about 420° F. contained some lepidine (the 20 carbon base, to be described further on), after four

more distillations it had gone higher up, and nearer to its correct boiling-point, and then the position in the series of fractions formerly occupied by a mixture of chinoline and lepidine became held entirely by the former.

Chinoline is the chief constituent of all the fractions boiling between 420° and 470° F. (216° to 243° C.) in the twelfth rectification; it is also contained in small quantity in the fractions a little below and above those points.

In a case like the present, where the chief means of separation was distillation, it was of course impossible to obtain the 18 and 20 carbon bases perfectly free from each other; and in bodies of so high an atomic weight, it was useless to attempt to prove their constitution by analyses of the bases themselves, as they only differ by 0.2 per cent. in the carbon, and when freed from those of the picoline series are extremely difficult to burn.

As no doubt exists of the constitution of the double salt formed with chloride of platinum, and as the salts of the two bases differ in the amount of carbon they contain by 2 per cent., and moreover are readily obtained pure, I availed myself of them to determine the fact of the existence of the two homologous bases in the fractions.

The properties of chinoline and lepidine approach so nearly, that one description will serve for both, less distinction being observable between them than is found to occur with a difference of $C^2 H^2$ in the other volatile bases.

It is remarkable to find bases boiling at such extremely high temperatures give such well-crystallized salts as those of chinoline and lepidine; even the portion boiling at 520° F. (271° C.) affords a fine platinum salt, almost insoluble in water, and without the slightest tendency to assume a resinous or oily condition, as the salts obtained from bases with such high boiling-points are so liable to do.

As chinoline has so long been known, although not in a state of purity, I was satisfied, for the purposes of the present investigation, with determining the composition of its platinum salt by the following analyses:—

	I.	II.	III.	IV.	V.			
Carbon	31.93	..	32.24	32.52	..	18=108	32.22	
Hydrogen	3.09	..	2.62	2.58	..	8	8	2.89
Nitrogen	..	..	..	..	..	1	14	4.18
Chlorine	..	..	..	..	..	3	106.5	31.77
Platinum	29.44	29.60	..	..	29.40	1	98.7	29.44

Lepidine—After repeated rectifications, it was found that the fraction boiling about 510° contained another base, to which I give the name of lepidine. It was only however when the rectifications had been very frequently repeated, that it was obtained pure. My reason for giving a new name to the base containing 20 eqivs. of carbon, and retaining that of chinoline for the other, was, that $C^{18} H^{17} N$ is almost universally received as the formula of the latter. It has been said that the positions of the bases in the fractions greatly alter as the rectifications proceed. This is nowhere more strikingly illustrated than with lepidine, which in the eighth rectifi-

cation was met with as low down as 420° F. (216° C.). By fractional crystallization, without heat, a crop was obtained, which yielded the annexed numbers:—

5.905 grs. of platinum salt gave 1.685 gr. of platinum = 28.53 per cent. Theory requires 28.27.

But this salt formed only a small portion of the original fraction, for upon further evaporation crystals were obtained, which the sub-joined platinum determination proved to consist of platinochloride of chinoline:—

6.345 grs. of platinochloride of chinoline gave 1.885 gr. of platinum = 29.71 per cent. Theory requires 29.44.

The real boiling-point of lepidine is probably as high as 500° F. (260° C.), or even a little higher; and after four more rectifications no sign of it could be found in the fraction at 420° F., and the nearest approach to a pure base was obtained at 510° F. (265° C.). But by so many distillations, at such an elevated temperature, it becomes slightly decomposed, a little pyrrole and carbonate of ammonia being formed; this, in addition to the incombustibility of the fluid, rendered its purification and analysis difficult. Fortunately however the same remark does not apply to its salts. On analysis it gave:—

Carbon	83.29	20 =	120	83.91
Hydrogen.....	6.57	9	9	6.29
Nitrogen	10.15	1	14	9.80

The above analysis, as regards the carbon, would be useless as evidence of the existence of lepidine, because, as has been said, the 18 and 20 carbon formulæ only cause a difference of 0.2 per cent.; but the hydrogen is so much higher in lepidine, that some slight judgement may be formed from the numbers obtained.

The platinum salt of lepidine contains 2 per cent. more carbon, and more than 1 per cent. less platinum than chinoline; and the analysis of that obtained from the fraction boiling between 510° and 520° F. (265° , 271° C.), which had been rectified no less than twelve times, gave the following result:—

I. and II. III. and IV.

Carbon.....	33.85	34.23	20 =	120	34.36
Hydrogen	2.94	2.96	10	10	2.86
Nitrogen	..	..	1	14	4.01
Chlorine	..	..	3	106.5	30.50
Platinum	28.18	28.08	1	98.7	28.27

As a further confirmation of the constitution of lepidine, the density of its vapour was ascertained with the following result:—

Temperature of balance case	58° F.
Temperature of vapour	551° F.
Excess of weight of balloon and vapour over balloon and air.....	10.050 grs.
Capacity of balloon	325.5 cub. centims.
Barometer	29.852 inches.
Residual air	0

Theoretical density of vapour.

 $C^{20}H^9N = 4$ vols.

4.94

Experiment.

5.14

Nitrate of Lepidine.—When the fraction boiling from 500° to 510° F. (260° to 266° C.) is dissolved in nitric acid of moderate strength, a solution of a pale red colour is obtained, which on evaporation yields a deep brownish-red, deliquescent, crystalline mass, which, on solution in water and re-evaporation, becomes lighter in colour. The nitrate in this state cannot be obtained in the form of a dry or pulverulent salt, in consequence of the presence of an impurity which renders it readily fusible at 212° . But if the salt is pressed repeatedly between folds of blotting-paper, and then crystallized from alcohol, fine hard prisms are obtained, quite infusible at 212° , and without the slightest tendency to deliquesce. As a little colouring matter was still retained, rendering the salt yellow, the crystals were pulverized and washed with æther, in which they were nearly insoluble; the purified salt gave, on combustion, the numbers annexed. It should be stated, that the first analysis was made upon a mixture of two crops, the second of which was obtained by evaporating the mother-liquor of the first; the second and third analyses were made upon the first crop of crystals:—

	I.	II.	III.	Mean.			
Carbon	57.69	58.40	58.24	58.11	20=120	58.25	
Hydrogen ..	4.93	4.90	4.98	4.93	10	10	4.86
Nitrogen ..	..	..	..	..	2	28	13.59
Oxygen	..	..	..	..	6	48	23.30

Hydrochlorate of Lepidine.—This salt is obtainable without difficulty in small white needles. The reason that former experimenters found so much time and trouble necessary to obtain crystals, was the presence of the more volatile bases, which, strange to say, yield crystalline salts with far greater difficulty than either chinoline or lepidine. The crystals of hydrochlorate of lepidine are quite infusible at 212° . An analysis gave a per-centage of 19.64 of chlorine. The formula $C^{20}H^{10}NCl$ requires 19.78.

Bichromate of Lepidine.—This extremely beautiful salt is easily obtained by adding an excess of a rather dilute solution of chromic acid to lepidine. For the first few seconds the chromate, on touching with a glass rod, appears resinous, but the instant it is stirred the salt becomes gritty and crystalline. On filtering off the crystalline powder obtained in this manner, and dissolving it in hot water, the salt crystallizes out on cooling, in needles nearly an inch long, extremely brilliant, and of a rich golden-yellow. The mother-liquors, on evaporation, yield a fresh crop. It does not appear to be at all decomposed by moderate boiling with excess of dilute chromic acid. It decomposes at no very elevated temperature, and if suddenly heated to 212° when slightly damp, it becomes converted into a mixture of green oxide of chromium and charcoal. On one occasion this took place with a very curious phenomenon. About 4 grs. in powder having been placed on a watch-glass, on the upper shelf

of the water-bath, it was not observed for about one hour, during which time it had become converted into a mass of flattened rods, reaching to the top of the water-bath, a distance of about $1\frac{1}{2}$ inch, and had turned down again on all sides, in a manner which gave the whole much the appearance of the capital of a Corinthian column. In general however it may be dried at 212° with perfect safety; if retained more than an hour or two in the bath, it begins to turn slightly brown, but experiences no further change during five hours' exposure. On ignition, the salt behaves like the bichromate of ammonia and the chromate of strychnine, inasmuch as it leaves pure green oxide of chromium. This fact enables the constitution of the salt to be determined with accuracy:—

	I.	II.	III.	IV.			
Carbon	..	..	..	47.05	20=120.0	47.36	
Hydrogen	..	..	..	3.89	10	10.0	3.95
Nitrogen	..	..	..	..	1	14.0	5.52
Chromium	21.17	21.28	21.35	..	2	53.4	21.07
Oxygen	..	..	..	..	7	56.0	22.10

Consequently the formula is $C^2H^2N + 2CrO_3 + 11H_2O$; and the salt analysed agrees with the bichromate of ammonia in only containing 1 atom of water.

Hydriodate of Amyl-lepidine.—On treating lepidine with iodide of amyle in a pressure-tube at 212° for some hours, a finely crystallized salt is obtained, rather sparingly soluble in water; it furnished 37.49 per cent. of iodine; hydriodate of amyl-lepidine requires 37.24.

Hydriodate of Methyl-lepidine is a finely crystallized body; but its history, and that of the analogous salt C^2H^2 below it, will be given in another paper, in which the leukoline of Hofmann will be compared with pure chinoline.

The experiments detailed prove therefore that cinchonine, by distillation with potash, yields pyrrole, pyridine, picoline, lutidine, collidine, chinoline and lepidine, a result which indicates a total breaking up of the cinchonine; and of this the appearance of pyrrole may be considered as a further confirmation, my experiments having shown that that substance is in general characteristic of the complex decomposition of nitrogenous substances.

When feathers, wool, or hair are distilled *per se*, sufficient pyrrole is evolved to give a reaction instantly with deal-wood moistened with hydrochloric acid, and as the experiment can be made in a test-tube, it serves very well for lecture illustration. Feathers yield a very large quantity of bases and carbonate of ammonia when distilled. The former appear, from my experiments (which as yet have only been on a very small scale), to contain some different from those at present known. Pyrrole possesses perhaps as high an interest as any basic substance obtained by destructive distillation; and it is singular that most nitrogenized bodies, when burnt with soda-lime, by Will and Varrentrap's process for determining the nitrogen, evolve pyrrole, which, passing through the acid in the

bulbs, may be recognized by the reaction with deal-wood and hydrochloric acid. Among the bodies tried in this manner, and found to give unequivocal reactions, may be mentioned guanos, dried turnips, oil-cake, hay and Para grass. Whether these facts prove a loss of nitrogen is at present doubtful, but the question will probably be solved when Dr. Anderson's researches on the pyrrole series of bases from Dippel's oil are completed.—*Transactions of the Royal Society of Edinburgh*, vol. xxi. part 2.

Simple Method of preparing the Protoxides of Iron, Manganese and Tin. By Prof. LIEBIG.

Prof. A. Vogel's description of the preparation of his excellent polishing powder from protoxalate of iron has been an inducement to the investigation of some other oxalates, especially the protoxalates of manganese and tin, which, as I have found, may be obtained perfectly anhydrous.

Protoxalate of manganese is obtained, like the iron salt, by precipitating a protosalt of manganese with free oxalic acid; it is a white pulverulent precipitate, with a tinge of red. When heated to 212° – 248° F., it loses all its water; and when heated in this state in a common combustion-tube, it furnishes carbonic acid and carbonic oxide gases in exactly equal volumes, and leaves a pure protoxide of manganese of a green colour, which, when touched with a red-hot body, ignites and smoulders into protoperoxide of manganese.

Protoxalate of tin behaves in exactly the same manner, and these two preparations may be employed in the formation of pure protoxide of manganese or tin as a class experiment. The decomposition of protoxalate of iron described by Vogel, furnishes a protoxide of iron which is not quite free from metallic iron, but which is at any rate the purest that can be prepared in an anhydrous state; it ignites spontaneously in the air, and burns like a pyrophorus to oxide of iron. Protoxalate of iron contains in 1 atom ($C^4O^6, 2FeO$) exactly 4 equivs. of water, as found by Vogel; when heated nearly to its point of decomposition, it loses another atom of water; and the great hardness of the oxide of iron obtained from it by slow combustion in the air depends evidently upon the dry combustion of the protoxide of iron.

I. 3.067 grms. of protoxalate of manganese, dried at 212° F., gave 1.642 gm. of protoperoxide = 50.02 per cent. of protoxide = (C^2O^3, MnO).

II. 3.941 grms. of protoxalate of iron, dried at 302° – 320° F., left after calcination 1.857 gm. oxide of iron = 42.4 per cent. of protoxide of iron; the formula $C^4O^6, 2FeO + 3Aq$ requires 42.11 per cent.

4.336 grms. of the same salt furnished 0.656 gm. of water = 15.03 per cent. (formula, 15.78 per cent.).

Protoxalate of iron, decomposed by itself in a tube, furnished on the average of four experiments 56 vols. of carbonic oxide, and 68 vols. of carbonic acid, instead of equal volumes.—Liebig's *Annalen*, July 1855, p. 116.

ANALYTICAL CHEMISTRY.

On Mohr's Volumetric Determination of Hydrocyanic Acid by Salts of Copper. By Prof. LIEBIG.

THIS method* for the determination of hydrocyanic acid by a solution of sulphate of copper, consists in mixing the hydrocyanic acid with ammonia, and adding a solution of sulphate of copper until the production of a blue colour; and Mohr assumes that under these circumstances the cyanide of ammonium is converted by the oxide of copper into oxide of ammonium and cyanide of copper ($2\text{CyNH}^+ + \text{CuO} = \text{CyCu} + \text{CyNH}^+ + \text{NH}^+ \text{O}$). This solution, however, contains no cyanide of copper (CyCu), but protocyanide of copper (CyCu^2); it is evident that under these circumstances the half of the cyanogen of the cyanide of copper first formed is got rid of, and it appears to me to be interesting to discover what becomes of this cyanogen.

I have poured ammonia over carbonate of copper and hydrated oxide of copper, and added hydrocyanic acid until all the oxide of copper was dissolved; the solution is effected without evolution of cyanogen; it is colourless, or of a slightly yellowish colour†. The solution was decomposed by finely-divided oxide of mercury, and boiled until the copper was precipitated, then evaporated to get rid of all the ammonia, and the cyanide of mercury formed was decomposed by sulphuretted hydrogen. If soluble products of decomposition had been formed by the action of the cyanogen separating from the cyanide of copper, they must be contained in this hydrocyanic fluid.

On evaporation and concentration, in fact, white crystals were separated; these were surrounded by a slimy mother-liquor, which at last solidified in a crystalline form. The crystals consisted of urea and oxalate of urea, which when treated with cold alcohol gave a solution of urea. The cyanogen of the cyanide of copper is consequently decomposed by free ammonia in exactly the same manner as has been described by Wöhler in passing cyanogen gas into liquid ammonia, only that under these circumstances no azulmic acid is produced.

The formation of urea or of cyanate of ammonia, of course, presupposes the simultaneous *production* of hydrocyanic acid, of which a portion, or even under certain circumstances the whole, may be decomposed into formiate of ammonia. It is clear that the formation of this must have an influence upon the method of determining hydrocyanic acid. I have, in fact, found that the quantity of copper solution required for the same quantity of hydrocyanic acid is not

* Chem. Gaz., July 2, 1855, p. 248.

† When this solution is mixed with a solution of hydrated oxide of copper in ammonia until it has become dark blue, crystals of a fine green colour separate, which on boiling become violet, without apparently undergoing any change of form.

always the same, but varies according to the quantity and concentration of the ammonia; when compared with my volumetric method by means of nitrate of silver, the copper solution always showed a little more hydrocyanic acid than was originally contained in the solution.

My silver solution contained 6·3 grms. of nitrate of silver in the litre, and indicated 2 milligrms. of hydrocyanic acid in 1 cub. centim. For the determination of hydrocyanic acid, a measured quantity of the latter is mixed with exactly 4 times its volume of water; and of this mixture 10 cub. centims. are mixed with potash, and the silver solution added until turbidity is produced. Each cubic centimetre of silver solution employed indicates 10 milligrms. of hydrocyanic acid in 1 cub. centim. of the undiluted acid. The copper solution was tested upon the silver solution; it contained 4·63 grms. of pure crystallized sulphate of copper in the litre.

10 cub. centims. of the diluted hydrocyanic acid required,—

Silver solution.	Copper solution.
12 cub. centims.	12·8 cub. centims.
12 ...	13·0 ...
12·2 ..	13·4 ...
11·9 ...	12·9 ...
Average. . 12·05 cub. centims.	13·02 cub. centims.

These experiments were repeated with the same result. As a general rule, the copper solution gave a greater amount.

With particular degrees of concentration, and in cases where the cyanogen is decomposed directly into oxalic acid, and the hydrocyanic acid into formic acid (which I have never recognized amongst the products of decomposition) and ammonia, the copper solution is, of course, fitted to furnish results as exact as those of the silver solution.—Liebig's *Annalen*, July 1855, p. 118.

On Chlorimetry. By C. NÖELLNER.

The general employment of chloride of lime as a bleaching and oxidizing agent, with its readiness to undergo change when long kept, and the variableness of its chemical composition even when apparently prepared in a similar manner, has given rise to a number of methods for determining its practical value.

Chemical manuals contain numerous methods for this purpose, generally founded on volumetric principles; Duflos alone, in his 'Theory and Practice of Pharmaceutical Experimental Chemistry,' proposes, by means of *sulphurous acid*, to form a quantity of sulphuric acid corresponding with the efficient amount of chlorine as a bleaching or oxidizing agent, and thus to determine it as sulphate of baryta by weighing.

Notwithstanding many advantages, this method has met with but little acceptance, probably because sulphurous acid is not much

employed in chemical laboratories; and, moreover, the aqueous solutions both of the free acid and its salts are converted by keeping into sulphuric acid and sulphates, so that when chlorimetric investigations only occur at considerable intervals, it is necessary to prepare this substance afresh upon each occasion, which will, of course, render the whole operation much too long for many.

All these disadvantages are got rid of by employing, instead of sulphurous acid, *hyposulphite of soda*, which is also converted into sulphate by free chlorine even at ordinary temperatures, and has hence been long employed for the removal of the last traces of chlorine from the stuffs bleached by it.

1 gm. of a sample of chloride of lime is mixed with about 2 grms. of hyposulphite of soda and water in a flask of such size, that when closed with a cork there shall be room enough left to allow of the complete diffusion of the chloride of lime by shaking, which is usually effected with ease. The complete conversion of the hyposulphite into sulphate takes place even in the cold, but for greater certainty the flask is heated a little in the water-bath. It is then mixed with a few drops of pure muriatic acid, or rather a sufficient quantity to make sure of the decomposition of all the excess of hyposulphite of soda, which takes place in the heated fluid immediately, with formation of sulphurous acid and sulphur. By inclining the flask and boiling for a few minutes, all the sulphurous acid is expelled, and the sulphur is deposited in drops exactly as in the decomposition of the metallic sulphurets by acids; so that on the complete decomposition of the excess of hyposulphite of soda, the fluid, which was at first milky and yellowish-white, becomes nearly limpid, and its separation from the melted sulphur by filtration is very easily effected, as is also the subsequent washing of the filter. The filtrate then contains the chloride of calcium of the chloride of lime, the excess of the muriatic acid added, and the chloride of sodium produced, together with a quantity of sulphate of soda exactly corresponding with the amount of oxidizing chlorine. This is precipitated with muriate of baryta.

As 16 of sulphur take up 8 of oxygen to form hyposulphurous acid, and the same 16 of sulphur must again take twice 8 of oxygen to be converted into sulphuric acid, for every 2 equivs. of chlorine 1 equiv. of sulphate of baryta, representing sulphuric acid, will be formed, and—

116.5 parts by weight (=1 equiv.) of sulphate of baryta will represent 71.5 parts (= 2 equivs.) of chlorine.

Hyposulphite of soda is unchangeable in the air, both in the solid state and in solution; and from its general employment, may be always obtained pure in commerce. Its conversion into sulphate by chlorine takes place readily, and its decomposition by muriatic acid gives origin only to sulphurous acid and sulphur without any sulphuric acid. Lastly, the sulphate of baryta formed is a compound which, when washed by decantation and afterwards on the filter, may be placed in the platinum crucible, dried, and heated to redness

without decomposition. From these circumstances, this method appears to be preferable to all others, as with a little practice it may be effected as rapidly as the volumetric methods, and with a certainty equal to that of the most exact analyses.

A good commercial sample of chloride of lime should furnish, according to the above method, at least its half of sulphate of baryta, which represents 30 per cent. of chlorine.—Liebig's *Annalen*, July 1855, p. 113.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Chemical Examination of some Hydraulic Limes. By C. KNAUSZ.

MANY limes have the property of becoming hydraulic by burning. This arises especially from the intermixture of clay and sand with the lime. Hence it cannot be doubtful, that not only the quantity of the clay, but also its composition and the temperature at which it is burnt, must have a considerable influence upon the goodness of the hydraulic lime produced. The author has investigated some English cements, exhibited by Messrs. Bayley, White and Son, in 1851. He was furnished not only with various English cements, including Portland cement, but also with the limestones from which they were prepared, and with the cubic blocks made from them. It might therefore be expected that he would arrive at conclusions as to what changes take place during the calcination of the limestone, and also during the hardening of the hydraulic lime. The author examined the following three limestones, four hydraulic limes, and four cubes prepared from them:—

I. Limestone from the county of Kent. It is of a yellowish-brown colour, tolerably hard, and containing an abundance of crystals of calcareous spar. It furnishes the so-called *Sheppey cement*.

II. Limestone from the county of Essex, of a similar appearance to the preceding. It furnishes the *Harwich cement*, of which No. V. is a sample.

III. Limestone from Yorkshire. It is bluish-gray, and harder than the other two. It furnishes the *Whitby cement*, No. VI.

No. X. is the analysis of Portland cement, from which the cube No. XI. was prepared. The cube No. VII. is of Sheppey cement; VIII. of Harwich cement; IX. of Whitby cement; and XI. of Portland cement.

In the following analyses, the portion soluble in muriatic acid and the insoluble residue are separately referred to. By quartz that portion of the insoluble residue which is not decomposed by sulphuric acid is intended. Silica is present partly in the soluble state, and partly rendered soluble by treatment.

A. Analysis of Kentish limestone, I.; of its cement, IV.; and the cube prepared from it, VII.:—

Insoluble in muriatic acid.	I.	IV.	VII.
Quartz	6.0	6.2	8.4
Silica	10.5	0.3	3.8
Oxide of iron	1.2	1.3	2.5
Alumina	2.5		
	20.2	7.8	14.7
Soluble in muriatic acid.			
Silica	0.7	19.4	8.1
Oxide of iron (with a trace of oxide of manganese)	11.6	9.2	6.6
Alumina	4.3	7.3	5.9
Carbonate of lime	52.4 CaO	48.2	42.8
Carbonate of magnesia	7.0 MgO	2.7	1.9
Potash	0.8	0.8	1.0
Soda	0.2	0.2	0.3
Water	2.8	1.0	6.9
	CO ²	3.4	11.8
	100.0	100.0	100.0

Analysis of Essex limestone, II.; cement, V.; and cube, VIII.:—

Insoluble in muriatic acid.	II.	V.	VIII.
Quartz	12.3	8.3	3.1
Silica	9.0	0.5	1.2
Oxide of iron (with a trace of oxide of manganese)	1.9	1.7	0.6
Alumina	2.4		
	25.6	10.5	4.9
Soluble in muriatic acid.			
Silica	0.6	17.4	17.6
Oxide of iron	6.3	12.4	9.5
Alumina	1.1	4.6	6.6
Carbonate of lime	57.8 CaO	46.1	36.6
Carbonate of magnesia	5.7 MgO	3.7	1.7
Potash	0.9	0.9	1.1
Soda	0.2	0.1	0.2
Water	1.8	0.7	8.3
	CO ²	3.6	13.5
	100.0	100.0	100.0

Analysis of Yorkshire limestone, III.; its cement, VI.; and cube, IX.:—

Insoluble in muriatic acid.	III.	VI.	IX.
Quartz	9.2	11.0	7.8
Silica	8.1	2.8	1.2
Oxide of iron	2.1	4.4	0.4
Alumina	3.8		
	23.2	18.2	9.4

Soluble in muriatic acid.			
Silica	0.5	9.1	9.2
Oxide of iron (with a trace of oxide of manganese)	2.3	7.1	6.1
Alumina	1.6	9.8	9.5
Carbonate of lime	68.7	CaO 49.6	40.0
Carbonate of magnesia	2.3	MgO 1.6	1.6
Potash.....	0.7	0.8	1.0
Soda	0.3	0.2	0.2
Water	0.4	0.9	8.6
		CO ² 2.7	14.4
	100.0	100.0	100.0

Analysis of Portland cement, X.; and its cube, XI. :—

Insoluble in muriatic acid.		X.	XI.
Quartz		8.1	9.8
Silica		0.5	0.5
Oxide of iron and alumina ..		0.8	0.3
		9.4	10.6
Soluble in muriatic acid.			
Silica	15.0	8.0	
Oxide of iron	4.5	2.6	
Alumina.....	6.5	3.3	
Lime	57.0	51.6	
Magnesia	2.5	1.8	
Potash.....	1.0	0.8	
Soda	0.2	0.1	
Water.....	0.4	3.2	
Carbonic acid.....	2.6	18.0	
	100.0	100.0	

B. If the ascertained analyses be calculated for the anhydrous state, and the wanting carbonic acid be added to the analyses of the cements and cubes, and the quartz, silica, oxide of iron, and alumina be taken together both in the soluble and insoluble portions, we obtain :—

	I.	IV.	VII.
Carbonate of lime	54.0	63.0	65.3
Carbonate of magnesia	7.2	4.2	3.4
Potash	0.8	0.6	0.8
Soda.....	0.2	0.2	0.2
Quartz, silica, oxide of iron and alumina	37.8	32.0	30.3
	100.0	100.0	100.0
	II.	V	VIII.
Carbonate of lime	58.8	60.5	60.0
Carbonate of magnesia	5.8	5.7	3.3
Potash	1.0	0.7	1.0
Soda.....	0.2	0.1	0.2
Quartz, silica, oxide of iron and alumina	34.2	33.0	35.5
	100.0	100.0	100.0

	III.	VI.	IX.
Carbonate of lime	69.0	64.6	64.9
Carbonate of magnesia	2.3	2.4	3.0
Potash	0.7	0.7	0.9
Soda.....	0.3	0.1	0.1
Quartz, silica, oxide of iron and alumina	27.7	32.2	31.1
	100.0	100.0	100.0
		X.	XI.
Carbonate of lime		70.5	75.9
Carbonate of magnesia		3.6	3.1
Potash		0.7	0.7
Soda		0.1	0.1
Quartz, silica, oxide of iron and alumina....		25.1	20.2
		100.0	100.0

These calculated results of Nos. IV. and VII., Nos. V. and VIII., and Nos. VI. and IX. agree so closely, that it may be admitted without scruple that Nos. IV., V., and VI. are the hydraulic limes which on hardening furnish the cubes VII., VIII. and IX.

The loss of the limestone during calcination amounts to about 30 per cent., whilst the hydraulic limes take up 12 to 15 per cent. of carbonic acid and about 8 per cent. of water during hardening.

According to these analyses, a limestone which will furnish a good hydraulic lime when burnt, requires to possess the following properties:—The amount of constituents insoluble in muriatic acid may form 20 to 30 per cent. of the limestone. The carbonates of lime and magnesia should amount to 60, or at the utmost 70 per cent. (the maximum of the carbonate of magnesia in the limestones examined was 7 per cent.). The remaining 10 to 20 per cent. are divided between iron, alumina and alkalies. In the limestones examined, the maximum of oxide of iron was 12 per cent., the minimum 2 to 3 per cent.; the alkalies were about 1 per cent.

Of the constituents which are insoluble in muriatic acid, three-fourths to five-sixths were gelatinous silica and quartz. In the limestone No. I. the gelatinous silica, in II. and III. the quartz is in excess; the gelatinous silica, however, even when it is present in the smallest proportion, forms one-third of the insoluble residue. The temperature necessary for the calcination no doubt depends on the amount of combined silica; a limestone will be more easily burnt in proportion as it contains more silicate, that is to say, silica united with oxide of iron and alumina in the form of clay. It appears however that the danger of too great a heat in burning limestones is much less than was formerly supposed, as the English hydraulic limes examined contained only very small quantities of carbonic acid; and the heat required for the complete expulsion of carbonic acid from limestones is far higher, and must be

longer continued, than is necessary for the decomposition of the silicate in clays.

The author also gives the analyses of two limestones from Horb in Wurtemberg, which furnish an hydraulic lime. I. and II. are the limestones, III. the hydraulic lime obtained from them :—

Insoluble in muriatic acid.	I.	II.	III.
Quartz	4.6	3.2	4.9
Silica	6.6	4.1	1.3
Oxide of iron	2.2	2.1	1.2
Alumina	2.5	1.8	1.3
	15.9	11.2	8.7
Soluble in muriatic acid.			
Silica	1.4	0.8	11.9
Oxide of iron	1.7	3.1	3.6
Alumina	3.1	0.8	5.6
Carbonate of lime	63.1	71.7	CaO 47.4
Carbonate of magnesia	12.3	9.3	MgO 9.4
Potash	0.8	1.1	1.5
Soda	0.4	0.3	0.3
Water	1.3	1.7	0.6
			CO ² 11.0
	100.0	100.0	100.0

These results, when calculated for the anhydrous state, and the carbonic acid added to the hydraulic lime (as under B), give,—

	I.	II.	III.
Carbonate of lime	63.9	72.9	62.2
Carbonate of magnesia	12.5	9.5	14.5
Potash	0.8	1.1	1.1
Soda	0.4	0.3	0.3
Quartz, silica, oxide of iron and alumina	22.4	16.2	21.9
	100.0	100.0	100.0

In comparison with the English limestones, they contain too little clay, and the hydraulic lime from Horb contains too much carbonic acid; it has not been sufficiently burnt.

The following is a method of comparing the value of different hydraulic limes, proposed by Prof. Pettenkofer of Munich. Of two hydraulic limes, which when free from air possess the same specific gravity, it will require very different quantities to fill the same space. The one of which a given bulk is the heaviest, is the best. A glass is filled with the different cements by knocking it on the table. By this means the author found that a glass which held 30.8 grms. of water, contained of the—

	English cements.	Weight of a cubic foot.
IV.	39.2 grms.	63.98 lbs.
V.	43.5	71.00
VI.	40.5	66.10
X.	52.5	

The same glass contained 37.9 grms. of the lime from Horb, giving 61.86 lbs. as the weight of a cubic foot.—*Gewerbebl. aus Württemberg*, 1855, No. 4.

Colour for marking Linen.

11 parts of nitrate of silver, 22 parts of liquid ammonia, 22 parts of crystallized carbonate of soda, 50 parts of gum-arabic, 2 parts of sap-green, and 13 parts of distilled water. The linen printed with this colour must be exposed for a long time to the sun-light, when it will appear sufficiently black. It is better to press it with a hot iron until the letters no longer increase in blackness.—*Mittheil. des Gewerbever. für Hannover*, 1855, p. 25.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 21, 1855. (The Lord Wrottesley, President, in the Chair.)

"On the Constitution and Properties of Ozone." By Thomas Andrews, M.D., F.R.S.

The conflicting views which have so long existed as to the true constitution of ozone, induced the author to undertake a careful investigation of the subject, particularly as he had reason to doubt the accuracy of the only quantitative experiments which have yet been made to elucidate this difficult question. According to the experiments referred to, two substances have been confounded under the name of ozone, one a compound body having the formula HO_3 , the other an allotropic variety of oxygen. To ascertain whether, in conformity with this statement, ozone obtained in the electrolysis of water contains hydrogen as a constituent, the author made two series of experiments. In the first series, he followed nearly the same method of investigation by which its compound nature is supposed to have been established, but modified so as to avoid a source of error, which, if neglected, vitiates altogether the results. Electrolytic oxygen, unless very great precautions be taken, is always accompanied by a small but appreciable quantity of carbonic acid, which is liable to be partially absorbed by the potassa set free when a neutral solution of iodide of potassium is decomposed by ozone. By adding a little hydrochloric acid to the solution of iodide of potassium before the commencement of each experiment, this error may be avoided.

The method of performing the experiment was to conduct a stream

of electrolytic oxygen through a compound apparatus previously weighed, which contained on one side an acid solution of iodide of potassium, and on the other sulphuric acid; the former to decompose the ozone, the latter to prevent the escape of moisture. The increase in weight of this apparatus gave the entire weight of the ozone; the iodine set free, when reduced to its equivalent in oxygen, the weight of the active oxygen. The precautions to be taken in conducting this experiment are fully described in the communication.

The following are the numerical results of five experiments performed according to the above method:—

Volume of electrolytic oxygen. litres.	Increase in weight of compound apparatus. grm.	Active oxygen deduced from iodine set free. grm.
10·20	0·0379	0·0386
2·72	0·0107	0·0100
2·86	0·0154	0·0138
6·45	0·0288	0·0281
6·80	0·0251	0·0273
Total	0·1179	0·1178

The agreement in these numbers proves that the active oxygen is exactly equal to the entire weight of the ozone, and is therefore identical with it.

In the next series of experiments the author shows that no water is produced in the decomposition of electrolytic ozone by heat. Large quantities of electrolytic oxygen, containing from 38 to 27 milligrammes of ozone, were decomposed by heat, but no water was obtained in a weighed absorption apparatus, in which the gas was exposed, not only to the action of sulphuric acid, but was also passed through a tube containing anhydrous phosphoric acid.

Having confirmed by new experiments the fact that ozone is formed by the action of the electrical spark on pure and dry oxygen, the author proceeds to institute a comparison between the properties of ozone derived from different sources. These he finds to be in every respect the same. Thus ozone, however prepared, is destroyed, or rather converted into ordinary oxygen, by exposure to a temperature of about 237° C., and catalytically, by being passed over peroxide of manganese, no water being formed in either case; it is not absorbed by water, but when sufficiently diluted with other gases, is destroyed by agitation with a large quantity of water; it is also, contrary to the common statements, destroyed by being agitated with lime-water and baryta-water, provided a sufficient quantity of those solutions be used; it has always the same peculiar odour; it bleaches without producing previously an acid reaction; it oxidizes in all cases the same bodies, &c.

From the whole investigation the author draws the conclusion, "that ozone, from whatever source derived, is one and the same substance, and is not a compound body, but oxygen in an altered or allotropic condition."

THE CHEMICAL GAZETTE.

No. CCCX.—September 15, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Fulminuric Acid. By J. LIEBIG.

DURING some experiments upon fulminate of mercury, I observed that this compound, when kept boiling in water, changed colour, and lost its fulminating properties.

In examining the changes which had taken place in the composition of the fulminate, I discovered a new acid, which has exactly the composition of cyanuric acid, but which differs entirely from that acid in the properties of the salts which it forms with the alkaline bases, salts which are very remarkable for the beauty and distinctness of their crystalline forms.

If we admit the formula $C^2 NO, HO$ as the equivalent of hydrated fulminic acid, the formation of the new acid is every easily explained. The elements of 3 equivs. of fulminic acid combine to form a single equivalent of the new acid, which I shall call *fulminuric acid*. 3 equivs. of fulminic acid $= 3(C^2 NO^2 H)$, form 1 equiv. of fulminuric acid $= C^6 N^3 O^6 H^3$:—

The formula of the potash salt is ..	$C^6 N^3 O^6$	$\left. \begin{array}{c} H^2 \\ K \end{array} \right\}$	
„ baryta salt	$C^6 N^3 O^6$	$\left. \begin{array}{c} H^2 \\ Ba \end{array} \right\}$	+ 2Aq.
„ basic lead salt ..	$C^6 N^3 O^6$	$\left. \begin{array}{c} H^2 \\ Pb \end{array} \right\}$	+ PbO.
„ ammonium salt	$C^6 N^3 O^6$	$\left. \begin{array}{c} H^2 \\ NH^+ \end{array} \right\}$	
„ silver salt	$C^6 N^3 O^6$	$\left. \begin{array}{c} H^2 \\ Ag \end{array} \right\}$	

The silver salt is soluble in hot water, and crystallizes in long silky needles.

The alkaline fulminurates are very easily prepared with fulminate of mercury, when this is boiled with an alkaline chloride. The fulminate of mercury dissolves at first, then two-thirds of the mercury is precipitated in the form of hydrated oxide, and the alkaline fulminurate remains in solution. By employing chloride of potassium, sodium or barium, a corresponding fulminurate, with potash, soda, or baryta as its base, is obtained. With chloride of ammonium the ammonia salt is obtained, the crystals of which are distinguished from all the others by a fine adamantine lustre; the crystals belong

Chem. Gaz. 1855.

to the clinorhombic system, and possess a double refraction of almost equal degree to that of Iceland spar. When exposed to a high temperature, they give rise to a slight deflagration.

The hydrated acid is easily obtained by decomposing the basic lead salt with sulphuretted hydrogen. It possesses a strongly acid reaction; when evaporated to a syrupous state, it gradually forms a crystalline mass, which dissolves in alcohol, and is converted into carbonic acid and ammonia by the action of acids.—*Comptes Rendus*, August 20, 1855, p. 293.

On Chlorine and Oxalic Acid. By M. HALLWACHS.

According to a statement of Döbereiner, dry oxalic acid absorbs chlorine gas, and forms therewith a white substance, which is decomposed by water into carbonic acid and muriatic acid, and should therefore be C^2HO^4Cl . This statement, which is repeated in all chemical manuals, is found to be incorrect by Hallwachs. According to his experiments, dry chlorine gas is entirely without action upon effloresced or sublimed oxalic acid, the quantity absorbed only corresponding with the porosity of the acid. If water be then poured over it, before the chlorine has been displaced by air, a slight evolution of gas takes place, because, as is well known, oxalic acid in solution furnishes muriatic acid and carbonic acid with chlorine.—Liebig's *Annalen*, xcv. July 1855, p. 120.

On the Root of Ononis spinosa. By Prof. H. HLASIWETZ.

[Concluded from page 325.]

Ononetine.—This body is obtained by diffusing onospine in about ten times its weight of water, heating it on a sand-bath until it is clearly dissolved, and then dropping in tolerably dilute sulphuric acid until the commencement of a slight permanent turbidity. If the fluid be now kept at a temperature near the boiling-point, a quantity of small clear drops are soon seen to form in it, and these increase and collect into a slightly yellow, heavy, oily mass at the bottom of the vessel. The supernatant fluid at length becomes clear again, and the decomposition is then complete. On cooling, the ononetine congeals into a crystalline mass, from which the fluid is poured away; it is recrystallized from strong alcohol, in which it readily dissolves.

The crystals are brittle prisms, often of great length, and united in tufts or in a radiate form; in operating with large quantities, they also acquire a considerable thickness and are highly refractive. They often occur grouped in a plumose form.

There is no advantage in employing concentrated acid in the decomposition of onospine, as with this a partial decomposition takes place. If a small quantity of onospine be heated in a test-tube with strong muriatic acid, it dissolves, and immediately afterwards the fluid is filled with small crystals of ononetine, which are of a brownish colour, and the fluid also acquires a reddish tint. With larger quantities, in this mode of decomposition, the ononetine also fuses into

large heavy drops, which are likewise strongly coloured. It is then difficult to purify the product by mere recrystallization, and even animal charcoal decolorizes it very slightly. But by proceeding as above described, the fused ononetine is at the utmost wine-yellow, and the supernatant fluid remains perfectly limpid.

This fluid contains sugar, which is readily obtained by adding freshly-precipitated pure carbonate of lead until all acid reaction is got rid of, filtering, treating with sulphuretted hydrogen to remove any traces of lead, and evaporating on the water-bath. When it is a little concentrated, a few crystals of ononetine may be thrown down, as this is not quite insoluble in water. After separating these by filtration and evaporating at a gentle heat, the residue is a very sweet syrup, capable of fermentation and crystallization, as to the nature of which no doubt can exist, as it perfectly exhibits all the reactions of sugar.

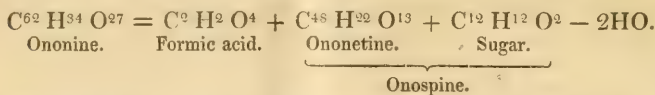
Properties of Ononetine.—When crystallized from alcohol it is almost insoluble in water. But when it is directly precipitated, as for instance from its alkaline solution by muriatic acid, and treated with a large quantity of water, a portion is dissolved, which on cooling fills the fluid with very shining interlaced needles. It dissolves in small quantity in hot æther. Alkalies dissolve it most readily. The ammoniacal solution, when exposed to the air, gradually acquires a fine dark green colour, resembling that of a solution of oxide of chrome. If muriatic acid be added to such a solution, a dark red, flocculent, resinous body is thrown down, which dissolves in alcohol with a splendid red colour. We are already acquainted with similar red resinous products from the decomposition of saligenine, phloretine and olivile.

Basic acetate of lead is the only metallic salt by which solution of ononetine is precipitated. Ononetine fuses at 248° F. without decomposition, and solidifies in a radiate crystalline form. When previously dried at 212° F., at which temperature it lost nothing in weight, it showed after fusion a loss of 1.86 per cent. of water. When heated upon platinum foil, it evolves a vapour provocative of coughing, afterwards burning with flame, and leaving a readily combustible coal. It is not sublimable.

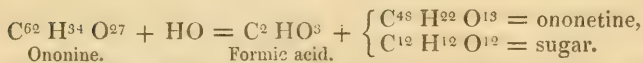
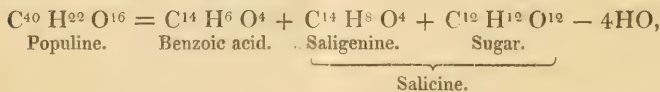
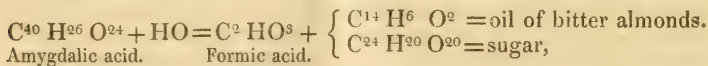
With sulphuric acid and oxide of manganese it exhibits the red reaction already mentioned under ononine and onospine; but in this case it is, if possible, more delicate. There is no doubt that both the above-mentioned bodies are indebted for this colour to the ononetine which they contain as a conjunct. The dark red reaction with chloride of iron is equally important. When heated with nitric acid, ononetine melts like a resin, and then becomes oxidized with evolution of an odour which acts severely upon the eyes, producing tears. The fluid contains oxalic acid, and apparently picric or oxy-picric acid. The analysis of the substance dried at 212° F. gave,—

	I.	II.	III.
C =	69.24	69.32	69.43
H =	5.71	5.59	5.88
O =	25.05	25.09	24.54

The author ascertained the amount of sugar in onospine by means of Fehling's test. The quantity is 30 per cent. according to several determinations. If these quantitative determinations be made use of in ascertaining the formulæ of these bodies, these and their composition appear to be as follows:—



Ononine has a certain degree of resemblance to amygdalic acid and populine:—



Besides ononine, the root of *Ononis spinosa* contains a second crystalline body, which may be very easily obtained, and the presence of which must be taken into consideration in the preparation of ononine, as otherwise it may readily contaminate the latter substance, particularly in two of the methods described.

When the root is extracted with alcohol, and the deep brown tincture is distilled until the residue has the consistence of a thin syrup, crystals are deposited in the course of a few days; these may be separated by a linen filter. They are still strongly coloured, but may be purified by pressing between paper, washing with cold alcohol, and solution in boiling alcohol. A considerable quantity of alcohol is required for this purpose, as they are difficult of solution. The yellow solution is deprived of a good deal of colour by animal charcoal, and on cooling and spontaneous evaporation acicular crystals are formed, which are obtained of a dazzling whiteness by repeated purification.

They are small, delicate, capillary crystals, which are interlaced together upon the filter, and diminish greatly when dried; they have a beautiful satin-like lustre; are very light, inodorous and tasteless; and when gently rubbed, become strongly electrical. They do not dissolve in water, and very little in æther, but alcohol dissolves them abundantly. The solution is precipitated by water, and this circumstance may be turned to account for the purification of the body.

When heated on platinum foil, they fuse without colour, and solidify in a crystalline form. When further heated, they diffuse an odour distantly resembling that of frankincense, burn with flame, and leave a readily combustible coal. They are free from nitrogen. The alcoholic solution has a neutral reaction, and gives no precipitates with metallic salts. Nitrate of silver is not reduced by boiling.

The crystals dissolve in concentrated sulphuric acid with a yellowish colour, and this is not changed by oxide of manganese. They are not altered by muriatic acid or solution of potash when boiled. They are insoluble in ammonia, but dissolve readily in hot oil of turpentine. Analysis gave:—

C.....	79·84	12 =	72	80·00
H.....	11·31	10	10	11·11
O.....	8·86	1	8	8·98

Behaviour with Chlorine.—When chlorine is passed over this substance at the ordinary temperature, it scarcely produces any change. But if it be placed in an apparatus which can be heated in the water-bath at the same time, evolution of muriatic acid commences immediately, the mass acquires a slight brown colour, and an amorphous, irregularly fused appearance. To render the action complete, the caking substance must be taken out several times, triturated, and again exposed to the chlorine. When the evolution of muriatic acid begins to diminish, the temperature of the bath is raised by chloride of sodium, and the operation is stopped when no more muriatic acid is given off.

The resinous mass thus produced was not soluble either in water or alcohol, but dissolved very readily in æther. After the evaporation of this solution, it remained in the form of an amorphous powder, which appeared white when it had been dissolved and evaporated three times. It is insoluble in ammonia and potash; in hot nitric acid it melts and becomes oxidized, and a solution of silver shows the presence of chlorine in the fluid; oxide of manganese produces no change of colour. On platinum foil it melts, and burns with an odour of resin and muriatic acid. The substance was dried at 212° F., and burnt with chromate of lead. The results were,—

C.....	57·4	12 =	72·0	57·8
H.....	7·1	9	9·0	7·2
Cl.....	27·5	1	35·5	28·4
O.....	8·0	1	8·0	6·6

1 equiv. of chlorine has consequently taken the place of H. If the pure substance be submitted to dry distillation with anhydrous phosphoric acid, an oil with a tar-like odour is produced. It is yellowish, but the author could not obtain it in sufficient quantity to purify and analyse it. It is probably a hydrocarbon = $C^{12}H^9$.

From its properties and behaviour this body stands in the neighbourhood of those neutral wax-like substances which have been prepared and described under the names of cerine, ceroxylene, cerosine, myricine, &c. It has also a great resemblance to the betuline of Hess; its per-centage composition is nearly the same as that of several resins, some kinds of wax, lactucone and worm-seed oil. The author denominates it *onocerine*.

The root also contains *citric acid*; it is combined with lime, and was obtained when the decoction of the root, which had been precipitated by acetate of lead, was freed from excess of lead by sulphuretted hydrogen, and slowly evaporated to the thickness of

The extract 2. consists of fatty oil, wax and chlorophyl, with traces of essential oil; 3. of yellowish-brown resin, osmazome, malate and muriate of potash, soda, lime and sugar; 4. of albumen, animal extractive matter, sugar, formiate, malate, phosphate, muriate, and sulphate of potash, soda, ammonia, lime and magnesia; 5. of gallate of iron, phosphate of lime, magnesia; 6. of humic acid, formed from animal fibre.—*Vierteljahrsschrift für Prakt. Pharm.*, iv. p. 321.

On Iodonitrate of Silver. By Dr. J. SCHNAUSS.

When a photographic layer on paper or glass is to be very sensitive, it must be arranged so that the light first passes through a stratum of nitrate of silver dissolved in water before reaching the iodide of silver in the collodion or paper. The author has found from experiment that there is a determinate compound of iodide of silver with nitrate of silver, which is obtained by dissolving dry iodide in a saturated solution of nitrate of silver, adding the former in small portions to the boiling solution until the latter is saturated. On the addition of water, this solution deposits iodide of silver. When it is allowed to cool, a salt separates in acicular crystals, the existence of which has already been mentioned by Preuss. As it is of importance in photography, the author has analysed it. Its composition is represented by $\text{AgO}, \text{NO}^5 + \text{AgI}$.

It rapidly becomes intensely black when exposed to daylight, far more so than its two constituents separately. It is not decomposed by absolute alcohol, and that fluid does not dissolve it even when boiling. Every drop of water added to it immediately decomposes a portion of the crystals, which then become coated with a yellow crust of iodide of silver. If a few pure fresh crystals be thrown into a beaker with distilled water, they become converted into iodide of silver whilst falling to the bottom, but retain their form. The only solvent for this compound appears to be a concentrated solution of nitrate of silver.

The author did not succeed in obtaining similar double salts by treating bromide and chloride of silver with a boiling solution of nitrate of silver. Bromide of silver indeed dissolves in very small quantity, and is also thrown down on the addition of water, but no crystalline compound is produced. This is perhaps the reason why negative photographs on bromide of silver alone are very weak and not sufficiently black.

The fluid poured away from the double salt which first crystallizes in needles, when allowed to stand for some time, deposits very regular distinctly-formed crystals of the same compound; these appear to be a combination of the octohedron with the hexahedron.

The above compound is always contained in the silver-baths of photographers after they have been used several times. Hence all these baths become turbid on the addition of water, from the separation of iodide of silver. A solution of nitrate of silver containing iodide of silver, that is to say an old bath, is however uni-

versally preferred by photographers to a freshly-prepared one; the latter may be artificially combined with a little iodide of silver.

The author has determined the solubility of nitrate of silver in water of 52° F., and found that 100 parts of fused nitrate of silver require 78.32 parts of water.—*Archiv der Pharm.*, lxxxii. p. 260.

Removal of Stains of Nitrate of Silver.

For this purpose the following solutions may be employed:—A solution of 8 parts of perchloride of mercury and muriate of ammonia in 125 parts of water, or one of 5 grms. of cyanide of potassium and 50 centigrms. of iodine in 45 grms. of water.—*Journ. de Pharm. d'Anvers*, October 1854.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of Phosphoric Acid, in the presence of the Alkalies, Alkaline Earths, Magnesia, Alumina, and the Oxides of Iron and Manganese. By J. WEEREN.

THE two methods proposed by Rose and Fresenius for this purpose take up a great deal of time, and require great expertness and perseverance; although this may be no valid objection to them, it will prevent the extended employment to which their excellence would entitle them. The attention paid to chemistry in the present day by agriculturists and manufacturers renders it advisable to render chemical analyses as simple as possible; and the author has therefore been induced to investigate this difficult subject, with a view to simplify the operations without losing sight of precision. His paper is as follows.

I. *On the Separation of the Alkalies, Alkaline Earths and Magnesia, by means of Oxide of Iron or Alumina.*

When to a solution of the phosphates of these bases in nitric acid, a solution of nitrate of alumina or iron, containing as much of the base as would be required by the phosphoric acid for the formation of the compounds produced by it under ordinary circumstances, is added, and the mixture is evaporated to dryness, and heated with a gradually increasing temperature as long as fumes of nitric acid are driven off, the residue contains the alkalies, alkaline earths and magnesia as *nitrates*, and the phosphoric acid in combination with oxide of iron or alumina. The nitrates may be extracted by repeated digestion with water and decantation, whilst the phosphoric acid, being combined with the alumina or oxide of iron into a nearly insoluble salt, remains behind. In this manner the alkalies and alkaline earths may be very easily separated with certainty from their phosphoric acid, and the residue may be heated to 482° F. without any fear of decomposition.

We are indebted to Chodnew for a very minute investigation of the decomposition of hydrated nitrate of magnesia at a high temperature, which furnishes the necessary data for the explanation of this anomalous behaviour. Thus whilst the nitrates of the alkalies and alkaline earths may be heated to a dull red heat without decomposition, the nitrate of magnesia loses its last atom of water at 464° to 482° F. together with a portion of its nitric acid, and passes into a basic salt. If nitrate of magnesia be evaporated with phosphoric acid and alumina or oxide of iron, this point is reduced still lower, which is particularly connected with the reduction of the basic properties of these bases at a high temperature and the action of the phosphoric acid thus set free upon the nitrate of magnesia, inasmuch as there is no doubt that alumina and oxide of iron more decidedly fulfil the part of acids the higher the temperature at which they are in contact with stronger bases. Numerous experiments have shown, that in separating phosphoric acid from magnesia on the above principle, a temperature of 347° to 356° F. must not be exceeded.

As I had expected this from the beginning, I turned my attention especially to the separation of phosphoric acid from magnesia, and only parenthetically to the alkalies and alkaline earths, particularly as I immediately obtained the most valuable results. This method necessarily presupposes the absence of all the stronger acids; for this reason the so-called pure commercial nitric acid must be rectified repeatedly when it is to be employed in this method. In all the experiments I proceeded in the following manner.

I prepared with the greatest care the nitrates of those bases which I desired to separate from phosphoric acid on the above principle, and employed these as test-fluids, the strength of which in the bases in question I determined by repeated experiments. In the same way I prepared solutions of oxide of iron and alumina in nitric acid, the strengths of which were also determined; it is not advisable in this case to use iron wire, for reasons which will be easily understood. Lastly, I prepared a test-fluid of repeatedly-crystallized *c*-phosphate of soda. Of the stability of the whole of the solutions during the series of experiments, I convinced myself by repeated analyses.

Of these fluids I usually mixed nearly equivalent quantities, taking as the basis the composition of the phosphates of the different bases, which would be formed under ordinary circumstances. I usually employed a solution of oxide of iron, as nitrate of iron is more easily prepared than the corresponding salt of alumina; and moreover the employment of iron presents some advantages, inasmuch as its nitrate is more readily decomposed than that of alumina, and the coloration of the dry residue, when iron is used, enables one to determine with greater ease whether the necessary excess is or is not present. Of this solution so much was usually taken, that its amount of iron corresponded with two or three times that of the phosphoric acid under examination; nevertheless 3 parts of oxide of iron may be employed to 2 parts of phosphoric, without giving rise to the least error.

The mixed solutions, which always contained so much nitric acid as to render the separation of the phosphate impossible, if it were insoluble in water, were evaporated to dryness on the water-bath, and then gradually heated to 320° to 338° F.; I endeavoured to keep a constant temperature of 320° F. For these experiments I made use of platinum capsules of about 2 inches in diameter, by which, although as they could not take the whole quantity of fluid at once the evaporation was at first rendered rather tedious, the subsequent determination of the weight was facilitated and rendered more certain. I obtained the higher temperatures exactly, and kept them constant even for a considerable time, by means of a spacious common air-bath. Of the removal of the whole of the nitric acid driven off at a certain temperature, I convinced myself by the gradual disappearance of the fumes, which were at first produced by liquid ammonia held on a glass rod near the upper aperture of the air-bath.

After the removal of the nitric acid, hot water was poured over the dry residue, which, if a solution of oxide of iron has been employed, should be of a bright ochre-yellow colour; it was then covered with a glass plate, and left for some time in a warm place to digest. The fluid was then carefully decanted into a beaker, and the residue again treated with water; this I repeated from four to eight times according to the quantity. The decanted fluid, which is seldom free from suspended particles of the precipitate, was boiled for some time, and poured, on cooling, through a small filter. The particles which adhered to the walls of the beaker were finally rinsed out with cold boiled water, and poured upon the filter.

If the above directions regarding the washing are followed exactly, there is no fear that the fluid will run turbid through the filter; this may also be effected without boiling the decanted fluid, but not with the same certainty of result.

I determined the bases dissolved in the filtrate by the best methods,—the magnesia by precipitation with ammonia and phosphate of soda; the lime in the form of oxalate; the baryta as sulphate; and the alkalies, after the evaporation and careful calcination of the filtrate, in the form of nitrates.

The filter, with the inconsiderable quantity of the precipitate which had been carried over, was dried and burnt in a platinum crucible; the platinum capsules with their contents, after the latter had been completely dried, were strongly heated. The difference between the weight of the contents of the platinum capsules and crucible and the known quantity of the oxide of iron or alumina, is equal to the amount of phosphoric acid contained in the substance analysed.

Analytical Proofs.

1. 0.5863 grm. of calcined phosphate of *soda* were evaporated to dryness on the water-bath with a solution of oxide of iron in an excess of nitric acid. The temperature of the air-bath was raised to 446° F. The experiment gave 0.3119 grm. of phosphoric acid

and 0·7484 grm. of anhydrous nitrate of soda, containing 0·2729 grm. of soda :—

	Calculated.	Found.
2NaO	46·62	46·55
PO ⁵	53·38	53·20
	100·00	99·75

Although subsequent experiments, in which, as already observed, a standard solution of phosphate of soda was constantly employed, sufficiently established the separation of phosphoric acid from soda upon this principle, I still give this experiment, in order, on the one hand, to prove the exactitude with which phosphoric acid is separated from the alkalies by this method, and also to justify the direct employment of phosphate of soda in all the following experiments, instead of a solution of phosphoric acid.

2. *Potash* may be separated from phosphoric acid by this method as certainly as soda.

3. The separation of nitrate of *baryta* also presented no difficulty. 0·3200 grm. of baryta and 0·5767 grm. of phosphoric acid gave 0·4880 grm. of sulphate of baryta, containing 0·3210 grm. of baryta and 0·5765 of phosphoric acid. The temperature was not raised above 356° F. :—

	Calculated.	Found.
Baryta	35·69	35·79
Phosphoric acid	64·31	64·29
	100·08	

4. An experiment made with nitrate of *lime* was not less favourable. The temperature was raised at last to 428° F. The solution employed contained 0·1472 grm. of phosphoric acid and 0·3000 grm. of lime. The experiment gave 0·1500 grm. of phosphoric acid and 0·7265 grm. of sulphate of lime, containing 0·2989 grm. of lime :—

	Calculated.	Found.
Lime	67·11	66·84
Phosphoric acid	32·89	33·54
	100·38	

The following experiment, which was made under the same conditions, led to a still better result. The solution contained 0·3229 grm. of phosphoric acid and 0·4123 grm. of lime ; the experiment gave 0·3218 grm. of phosphoric acid and 0·9995 grm. of sulphate of lime, containing 0·4116 grm. of lime :—

	Calculated.	Found.
Lime	56·08	55·99
Phosphoric acid	43·92	43·77
	99·76	

In all these experiments the quantity of oxide of iron was from two to three times as great as that of the phosphoric acid.

5. I did not attempt the separation of *strontia* from phosphoric

acid upon this principle, as there is certainly no doubt that it might be separated in this manner with as much certainty as baryta and lime.

6. With the separation of *magnesia* I did not at first succeed well, as I heated the mass evaporated to dryness in the water-bath at once nearly to the point of decomposition of nitrate of magnesia (428° to 466° F.); but it was readily separated from phosphoric acid by this method as soon as I had ascertained the conditions under which alone this can be effected with this base. From the numerous experiments which I might bring forward in confirmation of this statement, I have selected only a few; and in this case also, with but a single exception, I have only taken those in which a temperature of 320° to 336° F. was not exceeded. I must again state, that *under no circumstances should this temperature be exceeded*, as above this a partial decomposition of the nitrate of magnesia, and subsequently a combination of the base with the phosphoric acid takes place; and this is then either completely undecomposable, or only capable of incomplete decomposition by means of nitrate of ammonia or other reagents, unless by solution in nitric acid and repeated evaporation. In the separation of phosphoric acid from magnesia, I also prefer oxide of iron to alumina, as the nitrate of the latter is decomposed with rather more difficulty than that of iron.

The magnesia, as already stated, was separated in the form of phosphate of ammonia and magnesia. As this, as first ascertained by Otto, is particularly insoluble in liquid ammonia, I added to the filtrate containing the magnesia, after it was mixed with solution of muriate of ammonia and before the precipitation with phosphate of soda, a sixth or a seventh of its volume of liquid ammonia of spec. grav. 0.960, and washed the precipitate with an ammoniacal fluid which contained 1 part of gaseous ammonia to 60 parts of water.

0.2790 grm. of magnesia and 0.3238 grm. of phosphoric acid gave 0.7770 grm. of pyrophosphate of magnesia, which contained 0.2800 grm. of magnesia and 0.3276 grm. of phosphoric acid. The temperature varied between 284° and 356° F., but principally between 296° and 301° F. 1.0573 grm. of oxide of iron were added:—

	Calculated.	Found.
Magnesia	46.29	46.44
Phosphoric acid	53.71	54.34
		100.78

0.2817 grm. of magnesia and 0.4878 grm. of phosphoric acid furnished 0.7740 grm. of pyrophosphate of magnesia, containing 0.2807 grm. of magnesia and 0.4900 grm. of phosphoric acid. The temperature of the air-bath varied between 320° and 325° F., but the thermometer generally marked 320° F. For the separation of the phosphoric acid, 0.5800 grm. of oxide of iron were added; 0.5212 grm. of oxide of iron represents the amount of phosphoric acid employed, if the compound of the latter with oxide of iron

formed under ordinary circumstances is constituted according to the formula $\text{Fe}^2 \text{O}^3, \text{PO}^5$.

	Calculated.	Found.
Magnesia	36.61	36.48
Phosphoric acid	63.39	63.66
		100.14

I give another experiment, in which the temperature of the air-bath rose to 428°F. , and remained at this point for a considerable time, with the view of showing that a partial decomposition of the nitrate of magnesia took place:—

0.4261 grm. magnesia and	0.5680 grm. phosphoric acid
gave 0.3197	0.6705

Difference—0.1064 grm. magnesia and + 0.1025 grm. phosphoric acid

7. *Alumina*, as already stated, behaves in this respect exactly like oxide of iron, and may therefore, like this, be employed as a means of separation. As the establishment of the direct *empirical* proof of this appeared to me to be desirable on account of what follows, I give the result of the following experiment:—

0.2061 grm. of magnesia and 0.3656 grm. of phosphoric acid gave 0.5718 grm. of pyrophosphate of magnesia, containing 0.2055 grm. of magnesia and 0.3666 grm. of phosphoric acid; for the separation of the latter a solution of alumina in nitric acid was added, which contained 0.4603 grm. of anhydrous alumina. The solution of the nitrates was first evaporated to dryness in the water-bath, and then heated in the air-bath for some time at 248°F. , and afterwards between 302° and 320° , as long as fumes of nitric acid were driven off. The temperature rose once to 329°F.

	Calculated.	Found.
Magnesia	36.05	35.95
Phosphoric acid	63.95	64.12
		100.07

II. *General Process for the Separation of Phosphoric Acid from the Alkalies, the Alkaline Earths, Magnesia, Alumina, and the Oxides of Iron and Manganese.*

Although the above method can only find a limited application when the alkalies, alkaline earths, and magnesia are to be separated *singly* from phosphoric acid, as for this purpose there are other processes, which, if not more exact, certainly lead equally rapidly to the result, its value and applicability becomes immediately apparent, when the object is to separate phosphoric acid from these substances *in common*, or more especially from the above-mentioned bases when they occur in the presence of alumina, oxide of iron or manganese. In the former case, a known quantity of alumina or oxide of iron dissolved in nitric acid, corresponding with the amount of phosphoric acid, is added to the solution of the mixture in nitric acid; the nitric acid is driven off, as above described, at a temperature of 320° to

338° F.; the bases are separated by digestion with water from the residue, which contains the whole of the phosphoric acid with the alumina or oxide of iron, and from which the phosphoric acid is separated, as will be hereafter described. In the second case, if the quantity of alumina and oxide of iron contained in the substance be sufficient for the separation of the phosphoric acid, we have a sure means to divide the whole of the bases in question into two groups, one of which contains the alkalis, the alkaline earths and the magnesia, the other the alumina, the metallic oxides and the phosphoric acid. The former is separated by a process which will shortly be given; and even the latter may readily be decomposed into its constituents, as the bases contained in it may all be readily separated from the phosphoric acid, and afterwards from each other, either by fusion with carbonate of potash and soda and silica (on account of the presence of alumina), or by tartaric acid and solution of magnesia. If the quantity of oxide of iron and alumina be too small for the separation of the phosphoric acid, a sufficient known quantity of one or other of these bases is to be added. This is afterwards deducted from the amount of oxide of iron or alumina, ascertained in the analysis.

The following is the process which I adopt in the analysis of the above-mentioned bases. Only the purest nitric acid must be employed, and the presence of all other acids must be avoided. The dissolved mass is evaporated to dryness on the water-bath, and then exposed in the air-bath to a temperature gradually rising above that of boiling water, which is at last brought to 320° to 338° F., and this temperature is maintained as long as vapours of nitric acid are evolved. At this temperature not only the phosphates, but also the nitrate (?) of manganese, are completely decomposed; the latter becoming converted, even at 311° F., into peroxide of manganese, in which state, like the oxide of iron and alumina with the phosphoric acid combined with them, it is no longer soluble in water. The dry mass is then treated, as already described, with hot distilled water as long as anything is dissolved. In this manner a colourless solution (A) and a residue (B) are obtained; the latter is usually brownish-yellow, but in the presence of a compound of manganese shining black.

a. *Treatment of the Solution A.*

The solution contains magnesia, lime, soda and potash; the solvent is nitric acid. Nitrate of ammonia is added to it, and afterwards liquid ammonia free from carbonic acid, by which no precipitate should be produced; if a white precipitate be formed, it is usually from an insufficient quantity of nitrate of ammonia having been added, and it consequently disappears on a further addition of that salt; but if it be coloured, it indicates that the decomposition of the nitrates has not been complete, so that the solution must be evaporated and the process recommenced.

If the solution remain clear on the addition of the liquid ammonia, the lime is precipitated by oxalate of ammonia, the precipitate fil-

tered off after standing for half a day, and the lime weighed either as carbonate or sulphate.

The filtrate from the oxalate of lime is evaporated to dryness, and the residue brought gradually to a bright red heat, which is maintained for a considerable time. The non-volatile residue is treated with a concentrated solution of carbonate of ammonia, then evaporated to dryness, and strongly heated to redness. It may also be mixed directly with an excess of dry carbonate of ammonia, and the mixture calcined for some time, the temperature being raised gradually to a red heat. When the alkalies are thus converted into carbonates and the nitrate of magnesia into magnesia, the former are extracted by water, and the residue calcined and weighed; this gives the whole amount of magnesia contained in the substance. If traces of manganese have been separated with the magnesia, the calcined mass is dissolved in sulphuric acid; the manganese is then separated by the addition of muriate of ammonia and sulphuret of ammonium in the form of sulphuret; this is decomposed by muriatic acid, the manganese is thrown down from its solution by means of carbonate of soda, and weighed in the form of protoperoxide. The filtrate from the sulphuret of manganese is evaporated to dryness after the removal of the sulphuretted hydrogen and sulphur; the residue is carefully calcined, and the amount of magnesia calculated from the weight of the residue of anhydrous sulphate of magnesia.

According to Deville, this result may be obtained in a somewhat different way. The filtrate from the oxalate of lime is evaporated, and then exposed to a moderate red heat for the expulsion of the ammoniacal salts. Water is poured over the residue of nitrates, which are then evaporated to dryness with crystallized oxalic acid free from potash; this decomposes the nitrates, and converts them into oxalates, which, after they have been completely dried, are converted into carbonates by calcination. The alkalies are extracted with boiling water; the magnesia left, if it contain manganese, is treated with a hot concentrated solution of nitrate of ammonia, which, becoming decomposed, dissolves the magnesia, but leaves the manganese.

The alkalies, which in both cases are present as carbonates, are separated either by chloride of platinum after they have been converted into chlorides, or by indirect analysis.

b. *Treatment of the Residue B.*

This consists of alumina, oxide of iron, peroxide of manganese and phosphoric acid. The first thing to be done towards the separation of these bases is the removal of the phosphoric acid, which is best effected by melting the residue with carbonate of potash and soda to which a little silica has been added on account of the presence of the alumina.

After the removal of the silica, the best mode of separating the protoxide of manganese, oxide of iron and alumina, is to precipitate the two former by sulphuret of ammonium after the addition of tartaric acid and ammonia, decompose the metallic sulphurets by mu-

riatic acid containing nitric acid, and then separate the two by succinate of ammonia; the alumina is finally determined by the destruction of the tartaric acid, as recommended in my previous paper*.

The separation of the constituents of the residue might be still further simplified, if the method of separating phosphoric acid from weak bases, recommended by Otto, were sufficiently exact. But I have convinced myself by experiment, that in this method small quantities of phosphoric acid may be entirely overlooked; at least I found it impossible by its employment to ascertain even traces of phosphoric acid in some *black bands* from the Westphalian coal measures, in which I had found from a fourth to nearly one per cent. of that acid, by fusing the residue from the solution in nitric acid with carbonate of potash and soda.

If a substance contains, besides phosphoric acid, sulphuric and muriatic acids, acids which are certainly wanting in no soils, as they are always present in the ashes of plants, the process becomes rather more complicated. In this case I employ the following method.

The solution in nitric acid, which in this case must not contain too great an excess of acid, is first of all mixed with a measured volume of a *very dilute* solution of nitrate of baryta, containing a known amount of anhydrous baryta; care must be taken not to add more of this solution than is necessary for the separation of the sulphuric acid, although a slight excess is not very injurious. The sulphate of baryta is filtered off, quickly dried, calcined and weighed. From its weight the amount both of baryta and of sulphuric acid which it contains is calculated, and thus the amount of sulphuric acid contained in the substance under analysis is shown; it also furnishes the necessary data for calculating the quantity of baryta added in excess which still remains in the solution.

If the solution be afterwards evaporated, the fluid above indicated as A will contain baryta in addition to the bases mentioned, which may also, as I have stated at the commencement of this paper, be separated from phosphoric acid by the principle here employed. As the quantity of this baryta is known, it may be precipitated by the addition of an exactly equivalent quantity of sulphuric acid before the separation of the lime; and this is attended with no difficulty, if a sufficiently dilute solution has been employed. With the same result I have made use of a mixture of carbonate and oxalate of ammonia, by which the baryta and lime are thrown down together; these are then converted into sulphates, from which the quantity of sulphate of baryta corresponding with the known amount of baryta is deducted, so as to ascertain the quantity of sulphate of lime, from which the lime is calculated.

The separation of baryta and lime must be effected in the cold, as the carbonate of baryta which separates, although more difficult

* See Chemical Gazette, Aug. 15, 1855.

of solution than the corresponding oxalate, decomposes a solution of muriate of ammonia when hot, and thus dissolves.

Lastly, if muriatic acid be present, I add to the fluid filtered from the sulphate of baryta a sufficient quantity of a solution of nitrate of silver for the precipitation of the muriatic acid, which may be effected pretty easily, as chloride of silver separates so readily and quickly. But if an excess of the silver solution has been employed, I precipitate it by hydrocyanic acid, any excess of which is destroyed by the evaporation which takes place immediately after the filtration of the cyanide of silver.—Poggendorff's *Annalen*, xcv. p. 401.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 21, 1855. (The Lord Wrottesley, President, in the Chair.)

“On Rubian and its Products of Decomposition.”—Part III.
By Edward Schunck, F.R.S.

Combined Action of Alkalies and Oxygen on Rubian.

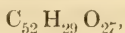
In the preceding part of this paper the author has shown that the action of alkalies is essentially the same as that of acids on rubian, the only difference being that the rubianine produced by acids is replaced by rubiadinine when alkalies are employed. Now though this is in all cases the final result of the action of alkalies, there still remained a possibility of the existence of bodies intermediate between rubian and the final products of decomposition. Such bodies do in reality exist, but their formation is dependent, in part at least, on the simultaneous action of oxygen.

When alkalies or alkaline earths, as potash, soda, ammonia, baryta or lime, or the bicarbonates of baryta or lime are added to a watery solution of rubian, and the solution is exposed to the air, oxygen is absorbed, and three distinct bodies are formed, to which the author has given the names of *Rubianic Acid*, *Rubidehydran* and *Rubihydran*. The method of separating these bodies and obtaining them in a state of purity is fully detailed. Even oxide of lead is a sufficiently strong base to cause rubian to undergo this process of decomposition in the presence of oxygen. From this cause the lead compound of rubian, after being exposed for some time to the atmosphere, no longer contains unchanged rubian, but products of its decomposition; and hence also it follows that in the processes proposed by Kuhlmann, Berzelius and others for the preparation of the so-called xanthine, and in that of Rochleder for the preparation of his ruberythric acid, all of which depend on the use of alkaline earths or basic acetate of lead, products of decomposition of rubian must in every case be formed. Besides the substances just mentioned, a little acetic acid, and sometimes also rubiadinine, and sugar in small quantities are formed. Whether the first is an essential product of decomposition or not, the author leaves undecided; but the other two

he considers as decidedly secondary products, resulting from the decomposition of rubidehydran or rubihydran.

Rubianic acid is soluble in water and alcohol, but not in ether. It crystallizes in lemon-yellow silky needles. Its watery solution has a distinctly but not strongly bitter taste. When heated it yields a sublimate of alizarine. By the action of strong acids, as well as of caustic alkalies and of erythrozym, it is decomposed into alizarine and sugar. Its compounds with potash and ammonia crystallize in small puce-coloured needles. The soda salt is deposited from the watery solution as a mass of small red spherical grains, which are very sparingly soluble in water. These compounds possess very little stability. The baryta and lime salts are obtained by double decomposition as red precipitates. The acid is completely precipitated from its watery solution by basic acetate of lead, the precipitate being red, and resembling that produced by the same salt in a solution of rubian.

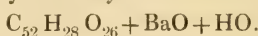
The composition of rubianic acid is expressed by the formula



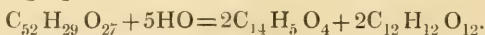
that of the potash salt by



that of the neutral baryta salt by



The conversion of the acid into alizarine and sugar is symbolized by the following equation:—



In order to leave no doubt regarding the correctness of the formula, the author determined the quantity of alizarine formed by the decomposition of the acid. According to calculation, 100 parts of acid should yield 43·44 parts of dry alizarine. In two experiments the author obtained 42·47 and 45·17 per cent. of alizarine.

The presence of oxygen is necessary for the formation of this acid. If a watery solution of rubian made alkaline with soda or baryta be kept out of contact with the air, no rubianic acid is produced, whereas an abundance of the latter is obtained from the same solution on exposure to the atmosphere. The manner in which it is formed from rubian may be represented by the following equation:—

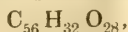


The author considers this as the first known instance of a body, belonging to the class of glucosides, or conjugate compounds containing sugar, having been observed to form by a process of oxidation.

The author thinks it probable that this acid and the ruberythric of Rochleder are identical, but the description given of the latter by the discoverer is not sufficiently minute to enable him to come to a decision on this point. Rochleder has moreover given a very different composition for his acid. Until the properties and composition of the latter have been more accurately investigated, the author

prefers considering the two acids as distinct. If they are identical, then Rochleder has merely committed the common error of mistaking a product for an educt.

Rubidehydran and rubihydran have both properties very nearly resembling those of rubian, from which they can only with difficulty be distinguished. Neither of them however is capable of yielding rubianic acid when treated in the same way as rubian. The composition of rubidehydran is expressed by the formula



that of rubihydran by

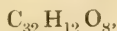


The former contains therefore the elements of 2 equivs. of water less the latter, the elements of 5 equivs. of water more than rubian. Both substances give, when decomposed by strong acids, the same products, viz. alizarine, rubiretine, verantine, rubiadine and sugar. The products formed by acids are therefore the same as those produced from rubian by alkalies, which renders it probable that the latter, when acted on by alkalies, is first converted into rubidehydran or rubihydran, or both.

Rubiadine may be obtained from rubihydran in large quantities and in a state of great purity, and the author had thus an opportunity of examining the properties and composition of this substance more accurately than heretofore. From the new analyses which he made he infers that its formula is



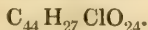
which differs from



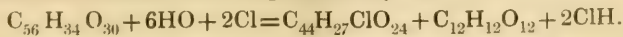
the one formerly given, by 1 equiv. of water.

Action of Chlorine on Rubian.

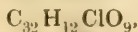
When chlorine gas is passed through a watery solution of rubian, the solution deposits lemon-yellow or orange-colour flocks and becomes colourless. The flocks consist of a peculiar substance, which the author calls *Chlororubian*. The liquid contains sugar. Chlororubian crystallizes from its solution in alcohol in small orange-coloured needles. It is soluble in boiling water, but not as easily as in alcohol. On being heated, however carefully, it is decomposed. It is dissolved by caustic and carbonated alkalies, forming blood-red solutions. The baryta and lime compounds are red and insoluble. The watery solution produces with basic acetate of lead a light red precipitate. The author gives for the chlororubian the formula



Its formation from rubian is represented by the following equation :—



Chlororubian is decomposed by strong acids and splits up into sugar and another body, which has the formula



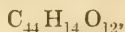
and which, in consequence of the relation in which it stands to rubiadine, the author calls *Chlororubiadine*. The manner in which this process of decomposition takes place will be seen from the following equation:—



Chlororubiadine is soluble in alcohol. The boiling solution deposits it on cooling in yellow shining needles. It is insoluble in boiling water. It is not decomposed by dilute nitric acid or on boiling, but nitric acid of sp. gr. 1.52 dissolves, and on boiling decomposes it, and nitrate of silver now gives a precipitate of chloride of silver. Chlororubiadine dissolves in caustic and carbonated alkalis with a red colour. With baryta it gives a compound, crystallizing in long red needles. The author did not succeed in converting rubiadine into chlororubiadine, nor, on the other hand, was he able to substitute the chlorine of the latter by hydrogen, and thus form rubiadine.

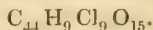
The sugar which is formed from chlororubian, together with chlororubiadine, may be obtained in a crystallized state, when it has the properties and composition of crystallized grape-sugar.

When chlororubian is treated with caustic soda, the chlorine is entirely separated, forming chloride of sodium. The other products of decomposition are verantine, rubiretine, a body resembling rubiadine, sugar, and a yellowish-brown substance insoluble in water, in alcohol, and even in alkalis, the probable formula of which is



and for which the author proposes the name of *Oxyrubian*, since it owes its formation to the chlorine of chlororubian being replaced by oxygen.

By the continued action of chlorine chlororubian is converted into a white body, which the author calls *Perchlororubian*. This body is insoluble in water and caustic alkalis, but soluble in alcohol and ether. It crystallizes from the alcoholic solution in colourless, transparent, four-sided tables, exhibiting a beautiful iridescence. When carefully heated it may be entirely volatilized. It is not decomposed by nitric acid of sp. gr. 1.52, even on boiling, but is merely dissolved. Its composition is expressed by the formula



From these experiments it follows that chlororubian is a conjugate body containing sugar. In this respect it resembles Piria's chlorosalicine.

In all the processes of decomposition previously described rubian yields three series of compounds, just as if it consisted of three bodies. When acted on by chlorine, however, it yields only one series of products, which corresponds exactly with one of the three series of the other processes, the bodies belonging to the two other series not making their appearance, even in the form of products of substitution.

THE CHEMICAL GAZETTE

No. CCCXI.—October 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on the Amides of the Fatty Acids. By THOMAS H. ROWNEY, Ph.D., F.C.S., Assistant in the College Laboratory, Glasgow.

THE following paper contains the details of some experiments upon the action of ammonia on the oils and fats, of which a preliminary notice was published in the Quarterly Journal of the Chemical Society of London*. The production of a soapy emulsion by the action of ammonia on these substances has long been familiar to chemists, but comparatively few accurate experiments have been made upon the compounds formed. Boullay † long since examined the crystalline substance obtained from olive-oil, which he called margaramide, and mentioned that similar compounds were obtained with the other oils, although he did not examine them. More lately ‡, M. Bouis produced ricinolamide from castor-oil, and showed that, by fusion with potash, it yielded caprylic alcohol and sebacic acid; and still more recently §, he has obtained another fatty amide, which he calls isocetamide, by the action of ammonia on the fat of the purging-nut of the West Indies.

From these experiments, it is obvious that the Glycerides of the fatty acids suffer the same decomposition when acted upon by ammonia, as their æthyle and methyle compounds undergo when exposed to the action of this reagent, amides being formed, and glycerine, methylic and æthylic alcohols being set free.

As the present communication contains a description of a considerable number of compounds obtained from different oils and fats, and as the method followed to obtain and purify them was nearly the same in all cases, I shall here describe it once for all, merely adding under each oil any particular remarks it may be necessary to make.

The compounds were obtained by mixing 1 part by measure of oil, 2 parts of alcohol, and 4 parts of strong solution of ammonia in a stoppered bottle capable of holding twice the quantity, and placed in a moderately warm situation, the stopper being tied with string,

* Quart. Journ. Chem. Soc. Lond., vol. vii. p. 200, 1855.

† Chem. Gaz., vol. ii. p. 236.

‡ *Ibid.*, vol. ix. p. 366.

§ *Ibid.*, vol. xii. p. 471.

in order to prevent its being blown out. The materials require occasional shaking, as, after standing some time, they separate into two layers, the oil depositing, and the alcoholic and ammoniacal fluid rising to the surface. After a certain time, varying with the nature of the oil employed, it becomes covered with a whitish solid matter, which gradually increases in quantity. The oil at the same time becomes thicker, diminishes in bulk, and finally both oil and ammoniacal liquor become nearly solid.

To purify the compounds, the pasty mass was collected upon a cloth filter, washed with water, and then squeezed, to free it as much as possible from the ammoniacal mother-liquor. The squeezed mass was then dissolved in warm alcohol, and allowed to crystallize, again filtered through cloth, and washed, first with dilute alcohol (made with equal parts of alcohol and water), then with water, and the residue again expressed; and this was repeated until it was obtained free from a resinous matter which adheres obstinately to it. When pure, these amides are perfectly white, and undergo no change by exposure to the air; but if any of the resinous matter adheres to them, they speedily change colour, becoming yellow and resinous. The alcoholic mother-liquors from which they have been crystallized retain a considerable quantity of the substances dissolved in them, which may be separated by the addition of water.

The original ammoniacal fluids, when evaporated on a water-bath, yield a considerable quantity of a dark oily or resinous matter mixed with some of the amide.

The quantity of the crystalline compound obtained from each oil varied very much, some yielding a considerable, and others a very small quantity. The time required for the completion of the action also differs; with some the change is readily and rapidly effected, but with others, and particularly with the drying oils, long-continued digestion is required. The latter oils yield a very small proportion of the crystalline compound, but a considerable quantity of resinous matter is obtained by evaporating the ammoniacal mother-liquors.

The quantities of substance employed for analysis were dried *in vacuo* over sulphuric acid, and the combustions were made with chromate of lead. The nitrogen determinations were principally made by Mr. Mitchell's modification of Peligot's method, viz. caustic soda, to neutralize the excess of sulphuric acid, infusion of logwood being used as the colouring matter.

The fusing-point was taken by placing a small quantity of the substance in a thin glass tube suspended in water contained in a metal vessel, which was heated by a gas-flame, and the temperature ascertained by immersing a thermometer in the water. When the fusing-point was found, the gas-flame was removed, the water allowed to cool, and the temperature at which solidification took place was also observed. In the case of the amide which fused at 103°C. , common salt was added, in small quantities at a time, so as to raise the temperature gradually until the fusing-point was obtained.

The following are the oils that I have already examined, and several others are in course of examination:—

Almond-oil, linseed-oil, poppy-oil, cod-liver oil, seal-oil and croton oil; also almond-oil and castor-oil, after solidification by nitrous acid.

Almond-oil is readily acted upon by ammonia, and yields a large proportion of the crystalline compound. This amide is very soluble in warm alcohol, and is deposited from the solution in mammillated groups of crystals. It is insoluble in water, and is separated from an alcoholic solution by dilution with water. It is not decomposed by boiling with a solution of potash, but fused potash decomposes it, with the evolution of ammonia.

It commences to fuse at 79°C. , and is completely fused at 81°C. When allowed to cool after fusion, it becomes solid at 78°C. , but remains semi-transparent.

The following results were obtained by analysis:—

	I.	II.	III.	IV.			
C	76.25	76.64	76.76	76.25	36 =	216	76.86
H	12.35	12.19	..	12.61	35	35	12.45
N	4.52	4.67	..	..	1	14	4.98
O	..	..	..	..	2	16	5.71

The ammoniacal mother-liquors, when concentrated, did not yield much resinous matter; but upon the addition of hydrochloric acid to the residue, an oil separated, which was collected upon a moist filter, and washed with water. It was then dissolved in ammonia, and chloride of barium was added; the precipitate obtained was filtered, and washed with water. I endeavoured to crystallize this salt from alcohol; but as it fuses into a resinous mass under the alcohol, and adheres to the sides of the vessel, it could not be satisfactorily accomplished. This property corresponds to that of oleate of baryta, and the analyses of it are sufficient to show that it was in fact this salt, although in an impure state.

The following are the results obtained:—

	I.	II.	III.			
C	..	..	60.51	36 =	216	61.78
H	..	..	9.49	33	33	9.44
BaO	22.28	22.56	..	1	76.6	21.91
O	..	..	..	3	24	6.87

Elaidine.—The solid fat obtained by passing nitrous acid into almond-oil is readily acted upon by ammonia, and yields a large quantity of a crystalline amide. Upon the addition of this reagent, a deep red colour is produced; and when the action is completed, the whole is transformed into a pasty mass, which is collected on a filter, washed with water, and expressed, by which means most of the colouring matter is removed, the mass is purified by several crystallizations from alcohol; and the amide is then obtained in brilliant groups of perfectly colourless crystals, which are very

soluble in alcohol but insoluble in water. Elaidamide is decomposed by fusion with potash, ammonia being evolved, but a solution of potash is entirely without action upon it. In this property it resembles oleamide; indeed all the fatty amides which I have examined agree in this respect.

It begins to fuse at $92^{\circ}\text{C}.$, and is completely fluid at $94^{\circ}\text{C}.$ Upon cooling, it solidifies at $91^{\circ}\text{C}.$, and becomes opaque.

The analysis gave the following results:—

	I.	II.			
C	76.72	76.16	36 =	216	76.86
H	12.68	12.72	35	35	12.45
N	..	4.88	1	14	4.98
O	..	..	2	16	5.71

Castor-oil.—I had commenced the examination of the action of ammonia upon castor-oil previous to the publication of M. Bouis's paper upon the same subject; but as he has described ricinolamide, and some of the products of its decomposition, I did not continue my own experiments in that direction, though I made a partial examination of the mother-liquor filtered from the amide.

When this filtrate is concentrated by evaporation, the addition of hydrochloric acid to it causes the separation of an oil, which was collected upon a moistened filter, washed with water, and then dissolved in ammonia. The addition of chloride of barium to this solution gave a precipitate, which was purified by repeated crystallizations from alcohol. It fuses under alcohol, and adheres to the bottom of the vessel, but is more readily soluble in alcohol than oleate of baryta. By analysis it was found to be ricinolate of baryta:—

	I.	II.	III.			
C	58.57	..	..	36 =	216	59.08
H	9.05	..	..	33	33	9.02
O	..	..	..	5	40	10.95
BaO	20.95	21.10	21.09	1	76.6	20.95

The cause of the presence of ricinoleic acid in the mother-liquor is explained by a remark made by M. Bouis in his paper, viz. that ricinolamide is decomposed by acids even in the cold. A small quantity of this amide must have been present in the mother-liquor, and been decomposed by the addition of the hydrochloric acid. The presence of oleic acid in the mother-liquor from oleamide may be accounted for in a similar manner.

Palmine, obtained from castor-oil by nitrous acid, when submitted to the action of ammonia, behaves in a similar manner to elaidine. A large quantity of amide is obtained, which is easily purified by crystallization from alcohol; and, when pure, it closely resembles elaidamide in appearance and properties.

It commences to fuse at $91^{\circ}\text{C}.$, is completely fused at $93^{\circ}\text{C}.$, and solidifies at $89^{\circ}\text{C}.$

By analysis the following results were obtained :—

	I.	II.	III.			
C	72.50	73.27	72.59	36 =	216	72.72
H	11.73	12.04	11.97	35	35	11.78
N	4.79	..	..	1	14	4.71
O	..	..	..	4	32	10.79

Linseed-oil requires long digestion with ammonia before it is acted upon, and it yields only a small quantity of amide, the greater portion of the oil being converted into a resinous matter, from which it is exceedingly difficult to purify the amide. It is insoluble in water, but very soluble in warm alcohol; and is deposited from this solution on cooling in mammillated groups of crystals, which when dry form a light, bulky, colourless, crystalline substance. The crystals soon acquire colour if they have not been thoroughly separated from the resinous matter. The fusing-point was found to be 100°C ., and it became solid again when cooled to 97°C .

The following results were obtained by analysis :—

	I.	II.			
C	75.31	75.18	34 =	204	75.83
H	13.03	13.01	35	35	13.01
N	5.01	5.04	1	14	5.20
O	..	..	2	16	5.96

These results correspond with the formula of margaramide, with which the properties of the substance also agree.

Poppy-oil is more readily acted upon than linseed-oil, and yields a considerable portion of amide, but also much resinous matter. The amide obtained is more easily purified than that from linseed-oil, but still repeated crystallizations from alcohol are necessary in order to free it from resin.

It is very soluble in alcohol, and crystallizes in mammillated groups. Its fusing-point was found to be 103°C .

The analysis of this compound shows that it also was margaramide :—

	I.	II.	III.
C	75.36	75.38	
H	13.01	12.93	
N	..	..	5.24

Croton-oil yields a small quantity of amide, and the mother-liquor, when concentrated by evaporation, contains a dark oily substance. The amide requires several crystallizations from alcohol to render it pure. It crystallizes in mammillated groups, and when dry is light and bulky. Its fusing-point is 100°C .

The analysis of this substance gave the following results :—

	I.	II.	III.
C	75.30	75.52	
H	12.78	13.04	
N	..	..	4.83

The nitrogen in this analysis is rather too low, and unfortunately I had no more substance with which to make another determination; but, however, the results altogether are sufficient to show that the substance was margaramide.

Seal-oil is readily acted upon by ammonia, and yields a considerable quantity of amide; the mother-liquor contains a large amount of resinous and oily matter, which separates by evaporation. The amide is readily purified by crystallization from alcohol, in which it is very soluble. When pure and dry, it forms a rather dense and crystalline powder, fusing at 82°C. , and is transparent when cold.

By analysis the following numbers were obtained, which correspond with those for oleamide, though the hydrogen is somewhat too high:—

	I.	II.	III.	IV.
C	76.74	76.65		
H	12.94	12.89		
N	..	..	5.02	4.85

Cod-liver oil requires to be digested for a considerable time with ammonia before it is acted upon. It does not yield very much amide, but a considerable quantity of an oily and resinous matter is obtained from the mother-liquor. It is very soluble in alcohol, and when dry presents similar appearances to the amides previously described; but its analysis gives results which at present I cannot explain, and on that account I have not given it either a name or formula. It fuses at 93°C. , and becomes solid and transparent at 91°C.

The following are the results obtained:—

	I.	II.	III.	IV.	V.
C	75.60	75.79			
H	13.03	12.95			
N	..	..	4.32	4.42	4.29

On comparing these results with those obtained from the other amides, it will be seen that the carbon and hydrogen would correspond with the formula for margaramide, but the nitrogen is nearly 1 per cent. too low; the fusing-point is also much lower than that of this amide. It likewise remains transparent when cold, which is a property belonging to oleamide, whilst the margaramide becomes opaque and somewhat crystalline when cold. It is my intention to make another examination of this oil, in order to ascertain the cause of these unsatisfactory results.

As it is my intention to continue this investigation, and also to examine the products of decomposition of these amides, I shall at present confine myself to a few remarks.

From the results of the analyses, it appears that linseed-, poppy-, and croton-oils yield margaramide, whilst oleamide is obtained from almond- and seal-oils; and, according to M. Bouis's experiments, ricinolamide is obtained from castor-oil; also from almond- and castor-oils, after solidification by nitrous acid, we obtain elaidamide

and palmamide, these amides being isomeric with oleamide and ricinolamide.

The only other point to which I shall refer is the temperature at which these amides fuse. M. Boullay states that the fusing-point of margaramide is 60°C ., but, according to my own experiments, I have found it to be as high as 103°C ., though in the cases of the amides from linseed- and croton-oils it was as low as 100°C ., but this arose from these substances not being perfectly pure; and it is probably a similar cause that occasions the error of M. Boullay. I am also inclined to think that the fusing-points of ricinolamide, 66°C ., and isocetamide, 67°C ., are too low. Isocetamide only differs by $2\text{C}^2\text{H}^2$ from margaramide, the fusing-point of which is 103° ; and ricinolamide is closely related to oleamide, which has a fusing-point of 82°C ., and the isomeric amides, palmamide and elaidamide, both fuse at about 94°C .—*Transactions of the Royal Society of Edinburgh*, vol. xxi. part 2.

On the Action of Heat upon Hydrated Oxide of Iron and Acetate of Iron. By L. PÉAN DE SAINT GILLES.

In a recent communication* the author pointed out the peculiar action exerted by prolonged heat upon a solution of acetate of iron, the chemical and physical characters of which undergo a complete change under this influence. For the explanation of this phenomenon, the author, by the advice of M. Thenard, has endeavoured to ascertain whether the facts observed are due only to a modification of the hydrated oxide of iron, or to a special reaction between the elements of this hydrate and those of the acetic acid, produced by the action of heat.

The employment of analysis being prevented by the difficulty of isolating the modified compound, he had recourse to synthesis. Having ascertained the transformation produced in a solution of acetate of iron by a heat of 212°F ., he inquired into the action produced by the same temperature upon free hydrated oxide of iron. This was prepared by the decomposition of chloride of iron, either by ammonia or bicarbonate of soda. The precipitate was washed repeatedly with cold water until it was entirely free from alkali, then suspended in water, and heated. After boiling for a few moments, the action commenced with a change in the tint of the precipitate, and caused it no longer to dissolve entirely in concentrated nitric and sulphuric acids. By continuing the application of heat in the salt-bath, the hydrate gradually acquired the brick-red colour which characterizes the modified acetate; and in this state not only acetic acid, but also diluted nitric and muriatic acids, cause the precipitate to disappear immediately, producing a liquid which is transparent by transmitted, but turbid by reflected light, and of a strong brick-red colour, and presenting all the characters of the modified acetate. The acetic acid consequently is not an essential element of the action.

* Chem. Gaz., vol. xiii. p. 165.

The following are the most important characters which distinguish the modified from the ordinary hydrate:—

1. The *modified* hydrate is insoluble in the cold in the most concentrated acids: even boiling nitric acid is almost without action upon it, so that it offers to a certain extent the characters of an indifferent oxide, whilst the *ordinary* hydrate is a readily salifiable base, which is dissolved by most acids even at a low temperature.

2. The *ordinary* hydrate, moistened with a mixture of ferrocyanide of potassium and acetic acid, is immediately converted into prussian blue; the *modified* hydrate undergoes no apparent change under these circumstances.

3. The *ordinary* hydrate, prepared and dried at the usual temperature, presents, when heated to a dull red heat, some remarkable phenomena of incandescence, to which Berzelius several times turned his attention. More recently M. Regnault has examined it in regard to its specific heat, and proved that that of oxide of iron is diminished by calcination, so that he is led to believe that the phenomenon of ignition corresponds with a sudden diminution in the capacity of the oxide for heat. It is certain that there is a very distinct line of demarcation between the two states of chemical activity and passivity of the oxide; the *modified* hydrate, however produced, never presents the phenomenon of incandescence, but behaves like the calcined passive oxide, with which it also agrees in colour.

The modified hydrate, heated to 212° F. for a certain number of hours, which varies according to the constancy of the temperature of the bath, loses the singular property of furnishing a red opaline liquid with certain acids. It would appear from this that this property corresponds with a certain definite degree of hydration. The precipitate by means of carbonate of soda, free from alkali and carbonic acid, presented exactly the composition Fe^2O^3 , $\text{HO} = 89.9$ per cent. Fe^2O^3 . This composition, which is also found in some natural crystallized hydrated oxides of iron, also occurred in several directly modified hydrates; but whenever the hydrate had lost the property of producing the opaline liquid with acetic acid, it contained less than 1 equiv. of water. This agrees also with the curious experiments of M. Senarmont, who not only succeeded in completely dehydrating hydrated oxide of iron, by heating it to 356° F. in a sealed tube, but has also decomposed chloride of iron, which at 482° F. furnished anhydrous oxide and muriatic acid.

The author adds, that from these facts it may be admitted that in the acetate modified by heat, the base has equally separated from the acid; but the temperature being less elevated, anhydrous oxide has not been produced, but instead of it the *modified hydrate*, Fe^2O^3 , HO , the most striking character of which is to furnish with acetic acid a liquid which is turbid by reflected, and limpid by transmitted light.

The alkaline acetates completely precipitate solutions of iron at the boiling-point; the precipitate is a mixture of basic acetate and modified hydrate. This shows how important it is, in the prepara-

tion of acetate of iron, to avoid the presence of all foreign salts. The most certain process is to dissolve the hydrocarbonate precipitated by pure carbonate of soda, and well washed in distilled water, in acetic acid free from sulphuric acid.

Hydrate of alumina, heated for a long time to 212° F., becomes like hydrated oxide of iron, insoluble in acids, and even in potash. This gives rise to a new comparison between the two bodies. Hydrated oxide of chrome, on the contrary, is not modified at the same temperature; when heated for twenty hours, it retained its original appearance, but was certainly less soluble in acids.

Acid solutions of iridium are precipitated at the boiling-point by the alkaline acetates; chloride of platinum does not present a similar reaction. This property may perhaps serve to separate iridium from platinum.—*Comptes Rendus*, June 11, 1855, p. 1243.

Notes on the Behaviour of Hyposulphite of Potash with certain Salts, &c. By J. W. SLATER, Esq.*

If hyposulphite of soda be added to chromic acid, rapid decomposition ensues, and the chrome is entirely precipitated as brown oxide, CrO_2 , whilst the supernatant liquid becomes colourless, containing sulphite and sulphate of soda. With bichromate of potash there is no immediate action, but on boiling, the brown oxide is deposited. The decomposition is not complete, the liquid containing chromates and sulphates of potash and soda.

The neutral chromate of potash is unaltered by hyposulphite, even on prolonged boiling; but if sulphuric, nitric, phosphoric, oxalic, citric, tartaric, or acetic acid be added, free sulphur is deposited, and the corresponding salt of chromic oxide formed. Hydrochloric acid, gradually and carefully added, causes brown oxide to be precipitated; but if applied in excess, it forms the sesquichloride.

The chlorate of potash is unaffected by boiling with hyposulphite, and crystallizes unchanged out of the solution, which gives no precipitate with salts of baryta.

The ferridcyanide of potassium is decomposed on boiling, with evolution of cyanogen and the deposit of a greenish-blue precipitate.

The ferrocyanide and cyanide of potassium yield, after long boiling, no precipitate, and do not show, as has been supposed, the least trace of sulphocyanides.

Metallic salts capable of precipitation with sulphuretted hydrogen, are completely precipitated when boiled with a slight excess of hyposulphite. This process appears in many cases preferable for analytical purposes to the use of sulphuretted hydrogen. The action is more rapid; there is less danger of other metals, such as zinc, being entangled in the precipitate; and the nuisance arising from free sulphuretted hydrogen is avoided.

If the solutions be cold, the results differ. Solutions of cupric salts, dilute or concentrated, undergo no further change than a disappearance of the green or blue colour. If acidulated with muriatic

* Communicated by the Author.

acid, there is also no immediate action; but on long standing, there appears a red shining deposit of sulphide of cuprous oxide in crystalline scales, adhering strongly to the sides of the vessel. ? ite

Sulphate of copper, dropped gradually into a solution of the hyposulphite, is entirely decolorized until a large excess has been added, when a yellowish-green colour appears. This change of colour is so marked, that a standard solution of the hyposulphite may be used for the volumetrical determination of copper.

Molybdates, if the base be one not precipitated by soluble sulphides, yield in the cold an olive-green liquid, which on boiling deposits the brown sulphide of molybdenum.

The arsenites and arseniates, when boiled, deposit their arsenic as sulphide. In the cold the action is barely perceptible, except the solutions be highly concentrated or a free acid be present. Hydrochloric acid determines a yellow precipitate of sulphide largely mixed with free sulphur; phosphoric acid, a dull yellow coloration, without precipitate; tartaric and citric acids, a yellow precipitate; acetic acid, a slight yellow precipitate, which redissolves on boiling; oxalic acid has no action in the cold; nitric and sulphuric acids throw down little beside free sulphur. The liquid in all cases retains traces of arsenic, unless a boiling temperature has been applied.

The chloride of antimony, as stated by Himly, yields a yellow deposit, which passes into scarlet (kermes) if the hyposulphite be in large excess and concentrated. If the latter is only moderately concentrated, a white precipitate is obtained, which is unchanged by ebullition, or by the addition of hydrochloric acid.

The nitrate of bismuth gives in the cold a greenish precipitate, chiefly sulphur; but on boiling, the metal is entirely thrown down as sulphide.

The soluble salts of lead yield in the cold a white precipitate (hyposulphite), which is easily soluble in an excess of the soda-salt. On boiling, the lead is completely precipitated as black sulphide.

Soluble salts of mercury form in the cold a white precipitate (a compound of sulphide of mercury with the original salt), which on agitation and exposure to the air gradually darkens. It was impossible to remove all the mercury from a solution without the aid of heat. On one occasion, after the first dark precipitate had been filtered off, a fresh white deposit, formed on the addition of a further quantity of hyposulphite, which had stood for a night without undergoing any change, passed rapidly on the application of heat into the crystalline scarlet sulphide, or vermillion.

The sulphocyanide of iron, dropped into a solution of hyposulphite, is decolorized until a large excess has been employed. No volumetrical procedure could, I think, be founded upon this reaction, since the change of tint, as saturation approaches, is exceedingly gradual.

The red permanganate of potash is reduced to the green manganate in contact with hyposulphite, and the solution of the manganate passes in a short time into a vinous red, from which on

standing, or the application of heat, all the manganese is deposited as hydrated peroxide.

A cold highly-concentrated solution of hyposulphite dissolves the following substances:—Chlorides of lead and mercury (calomel), when recently precipitated; iodides of silver, mercury (abundantly), lead (more sparingly), copper and bismuth; cyanides of lead, copper, silver, uranium, zinc, manganese (imperfectly), cobalt (very imperfectly), cadmium and bismuth; ferrocyanides of copper, lead, silver, iron (slightly), uranium (solution a claret-red), cobalt and bismuth; ferridecyanides of copper, silver, manganese, cadmium and lead. The ferrocyanides of manganese, cadmium, and zinc were not dissolved.

The ferridecyanide of uranium is precipitated as a deep maroon powder, and that of cobalt is blackened without solution.

Of these solutions, some undergo spontaneous decomposition, but others appear stable, and may yield definite crystalline compounds. The solutions of chlorides are less stable than those of the iodides.

Sheffield Mechanics' Institution,
Sept. 22, 1855.

On the Artificial Preparation of Alcohol. By M. MARX.

Berthelot has lately stated, that alcohol may be formed from olefiant gas. Marx shows that this discovery was made twenty-seven years ago by Henry Hennell. In the Philosophical Transactions for 1828, p. 365, there is a theory of the formation of æther, in which Hennell says, "This theory is illustrated by the employment of olefiant gas as the hydrocarbonous base; for, by combining this gas with sulphuric acid, we may form sulphovinic acid, from which we may obtain at pleasure, by varying the circumstances of the decomposition, either alcohol or æther."—*Journ. für Prakt. Chem.*, lxx. p. 92.

On Hydrated Silica and Silicate of Ammonia. By J. LIEBIG.

According to some experiments of Liebig, the solubility of silica in water depends essentially upon the circumstance whether or no a sufficient quantity of water for its solution is present at the moment that it is separated from an alkaline silicate. If a sufficient quantity of water be present, a much larger quantity of silica dissolves than when water is saturated with gelatinous silica.

If a solution of soluble silicate, the strength of which per cubic centimetre is known, be gradually diluted with measured quantities of water, a point may be arrived at when, on the addition of an acid (muriatic acid) in slight excess, the fluid remains perfectly clear, and no silica is separated. From experiments it appears that by this process water will dissolve as much as $\frac{1}{5000}$ dth of silica.

Ammonia, like carbonate of ammonia, diminishes the solubility of silica in water; for when a few drops of ammonia have been added to the solution above described before the addition of acid, a

fluid is obtained, which does not remain clear, but becomes opalescent, and finally gelatinous. Muriate of ammonia produces the same effect. A solution of carbonate of ammonia, added to the above-described clear fluid after the addition of the acid, even when this has been diluted with double the quantity of water, causes it to become opalescent, and even to coagulate. The former appearance is produced even after the addition of a few drops of the solution of carbonate of ammonia; the latter, when the quantity added amounts to about one-eighth of that of the solution of the silicate.

From Liebig's experiments it appears that no chemical compound of silica and ammonia exists; the ammonia found by Struckmann in gelatinous silica is retained by this in the same manner as by porous bodies, such as alumina.

Way has observed (*Journ. Agric. Soc.*, xii. p. 124) that clay, which, as is well known, absorbs ammonia, also possesses the power of extracting the ammonia from water containing it. This property, says Liebig, explains why drainage-water seldom, if ever, contains traces of ammonia; the ammonia is not washed out of fields with a clayey soil. Way has explained this by the supposition, that ammonia, like lime, is capable of entering into the composition of the double silicate of alumina and lime contained in the soil, by displacing the lime; he has also expressed the opinion, that such double silicates of alumina and ammonia furnish plants with the ammonia required for the production of their nitrogenous constituents. Liebig expresses himself very decidedly in opposition to this explanation of the fact, the silicates of alumina absorbing ammonia like other porous bodies (*sea-sand, asbestos, Faraday*), and also against this supposed source of nitrogen for plants.—Liebig's *Annalen*, xciv. p. 373.

On the Preparation of the Solution of Chloriodide of Zinc as a Reagent for Microscopic Investigations. By Dr. L. RADLKOEFER.

Prof. Schulze of Rostock first recommended the employment of the solution of chloriodide of zinc for the treatment of microscopic objects. The prescription given by Schacht for the preparation of this reagent, furnishes a preparation, which, according to the author's statements, is not always uniform. The following is the author's process:—

A solution of nearly pure chloride of zinc is first to be prepared. For this purpose muriatic acid is treated with an excess of zinc; the excess of zinc in this case throws down any metals by which it is contaminated. The solution is evaporated at a temperature but little exceeding that of boiling water, and thus a fluid of a density of about 2.0 is obtained; this possesses all the known properties of a nearly pure chloride of zinc.

This solution is diluted with water until its density is 1.80. If its original density was 2.0, 12 parts by weight of water are required for 100 parts of solution. In 100 parts of this fluid, 6 parts by weight of iodide of potassium are dissolved with the aid of a gentle

heat, and it is then heated with an excess of iodine until the latter is no longer dissolved, and violet fumes are perceptible over the fluid.

The reagent has the consistence of concentrated sulphuric acid; it is perfectly clear, and of a pale yellowish-brown colour. It communicates a violet or blue colour to vegetable cellulose membranes, without dissolving them gradually. It colours the fibres of raw cotton bluish-violet, and the parenchyma of the Aloe leaf a pure and deep blue.

When employing this fluid, it is necessary that the microscopic objects should be previously soaked in water. The solution itself must be kept well stopped, as otherwise it loses iodine. Dilution with water causes the coloration produced by it to be more violet. A greater addition of iodide of potassium and iodine produces more of the brown colours, which are caused by iodine alone. It follows from this, that for the action of the reagent to be uniform, the concentration above recommended should be obtained as nearly as possible. The density of the solution of chloride of zinc should never exceed 1.90, or fall short of 1.75.—Liebig's *Annalen*, xciv. p. 332.

On the Decomposition of Insoluble and nearly Insoluble Salts by the Alkaline Carbonates. By H. ROSE.

The author has already shown in what manner the sulphates of baryta, strontia, and lime behave towards the alkaline carbonates. Sulphate of lead in this respect resembles the two last salts, for it is completely decomposed, and converted into carbonate of lead, by solutions of the alkaline carbonates and bicarbonates, even at ordinary temperatures. The solutions of the neutral alkaline carbonates dissolve a little of the oxide of lead, but this is not the case with the bicarbonates. By means of solutions of the latter salts, sulphate of lead may be quantitatively separated from sulphate of baryta; this is best effected by a solution of commercial carbonate of ammonia, which always contains bicarbonate.

Carbonate of lead is not converted into sulphate of lead by solutions of alkaline sulphates, either at ordinary temperatures or by boiling.

Chromate of Baryta behaves towards solutions of alkaline carbonates somewhat like sulphate of baryta, although differing from it in several respects. Thus it is decomposed by neutral alkaline carbonates even at ordinary temperatures. If the yellow fluid be then poured away, and replaced by a fresh solution of the alkaline carbonate, and this operation be repeated several times, a complete decomposition may be effected, and the chromate of baryta is at last entirely converted into carbonate. This is effected with far more ease and rapidity when an excess of a boiling solution of the alkaline carbonate is employed. If equivalent proportions of chromate of baryta and carbonate of soda be boiled with water, 1 atom of the former is decomposed by 7 of the latter; but if the two salts be fused together, and the fused mass treated with water of the ordinary tempera-

ture, it is remarkable that only 1 atom of chromate of baryta is decomposed by 21 of carbonate of soda.

The decomposition of chromate of baryta by solutions of alkaline carbonates is completely prevented when a sufficient quantity of neutral alkaline chromate is added to the latter. Not the smallest portion of carbonate of baryta is then produced, even by boiling. On the other hand, carbonate of baryta is completely converted into chromate of baryta, by treating it with a sufficient quantity of a solution of a neutral alkaline chromate.

Seleniate of Baryta is readily and completely decomposed by a solution of an alkaline carbonate, even at ordinary temperatures. It is thus essentially distinguished from sulphate of baryta. The author has however convinced himself that seleniate of baryta is not perfectly insoluble in water, which may explain its behaviour towards the alkaline carbonates.

Oxalate of Lime, like chromate of baryta, is decomposed by solutions of alkaline carbonates at ordinary temperatures. The fluid must be frequently poured away from the undissolved portion, and replaced by a fresh solution of the alkaline carbonate, in order to effect complete decomposition. This however is very rapidly produced by boiling the oxalate of lime with the solution of the alkaline carbonate; but it is entirely prevented when the oxalate of lime is treated with a solution of carbonate of potash to which a sufficient quantity of oxalate of potash has been added, either at the ordinary or at elevated temperatures.

If equivalent proportions of oxalate of lime and carbonate of potash be treated with water at the ordinary temperature, only 2 atoms out of 17 are decomposed; but if the whole be boiled, 5 atoms out of 8 of the oxalate of lime are decomposed, and converted into carbonate of lime.

If carbonate of lime be treated with a solution of neutral oxalate of potash at ordinary temperatures, it is partially converted into oxalate of lime; if it be boiled therewith, oxalate of lime is more rapidly produced, but it does not appear to be possible to convert the whole of the carbonate of lime into oxalate, even by frequently pouring away the fluid and replacing it by a fresh quantity of oxalate of potash.

Oxalate of Lead is completely decomposed by a solution of an alkaline carbonate, even at ordinary temperatures, and becomes converted into carbonate of lead, of which however a small quantity dissolves in the alkaline fluid.

From these and the other, certainly not very numerous, examples of the decomposition of insoluble and nearly insoluble salts by soluble salts, the author draws the conclusion, that where the decompositions do not agree with the commonly received laws of affinity, this is owing principally to the soluble salt formed being capable of decomposing the insoluble salt produced; thus the whole decomposition is hindered, and this hindrance can only be got rid of by the removal of the soluble salt, and its replacement by a new solution of the decomposing salt. When no such decomposing action of the

resulting soluble salt upon the insoluble one takes place, the decomposition goes on in accordance with the ordinary laws of affinity. As an alkaline carbonate decomposes sulphate of baryta in the same manner that an alkaline sulphate decomposes carbonate of baryta, only a very imperfect decomposition can be produced by equivalent weights of an alkaline carbonate and sulphate of baryta, or of an alkaline sulphate and carbonate of baryta. As however an alkaline carbonate can decompose sulphate of strontia, but an alkaline sulphate has no effect upon carbonate of strontia, a nearly complete decomposition is produced in the former case, when equivalent weights of the substances are employed. For the same reason a nearly complete decomposition takes place with equivalent proportions of an alkaline carbonate and sulphate of lime or lead.

That in these cases the resulting compound of carbonic acid with strontia, lime, or oxide of lead is not decomposed by the alkaline sulphate produced, is connected with the solubility of the sulphates of strontia, lime and lead, small as this is; for if the smallest quantities of these sulphates were to be formed, and dissolved in the fluid, they could not resist the decomposing action of the alkaline carbonate produced at the same time.

But although in the decomposition of completely insoluble salts, as for instance sulphate of baryta, by soluble ones, such as alkaline carbonates, the decomposition is principally hindered by the opposite action of the soluble salt produced upon the insoluble one, this hindrance cannot be the only one. The author formerly regarded the affinity of the soluble alkaline sulphate for the still-undecomposed sulphate (of baryta) as the most important hindrance to the decomposition. But although this affinity undoubtedly has an injurious action, it cannot be the principal hindrance, as a similar affinity exists between the alkaline sulphates and the sulphates of lime and strontia. We are even acquainted with the compounds of these two salts with sulphate of potash in the crystalline form, whilst a solid compound of an alkaline sulphate with sulphate of baryta is still unknown, and this must consequently be more difficult of formation and more readily decomposed by water than the others. But the affinity of the alkaline sulphate for sulphate of lime or strontia has a less injurious effect upon their decomposition by alkaline carbonates; it can only be observed in general where equivalent weights of the salts are employed, and is readily overcome when the alkaline carbonate is employed even in slight excess. From the preceding investigations it appears that very different results are obtained in the decomposition of sulphate of baryta by alkaline carbonates at different temperatures, by boiling with water or by fusion.

Chromate of baryta and oxalate of lime behave towards the alkaline carbonates for the most part in the same, or at all events in a similar manner to sulphate of baryta. These are salts which we regard as insoluble in water, and which, precisely because they are insoluble in water, resist decomposition by an equivalent weight of an alkaline carbonate. And this constitutes exactly the distinction

between these insoluble salts and those which are only very difficult of solution; the latter are almost, if not quite, completely decomposed by an equivalent weight of an alkaline carbonate, and a slight excess of the carbonate is always sufficient to cause the entire decomposition.

All insoluble salts do not however behave towards solutions of alkaline carbonates like sulphate of baryta, chromate of baryta and oxalate of lime. Thus there are many insoluble phosphates which resist complete decomposition by alkaline carbonates with great obstinacy, when the same process is applied to them, which readily produces the entire decomposition of sulphate and chromate of baryta and oxalate of lime.—*Ber. der Akad. der Wiss. zu Berlin*, 1855, p. 388.

On the Iodonitrate of Silver. By C. WELTZIEN*.

A hot concentrated solution of nitrate of silver dissolves iodide of silver, and, on the cooling of the fluid, acicular nacreous crystals of iodonitrate of silver are formed. On the addition of water, both the solution and the crystals are decomposed, iodide of silver being separated.

J. Preuss has already referred to this compound, but without stating anything as to its composition. I have had it analysed by my assistants. The analysis gave,—

	Found.		Calculated.
	I.	II.	
AgI	40.4	40.0	40.8
AgO NO ⁵	58.3	58.99	59.2

The formula is consequently AgI + 2AgO, NO⁵.

This solubility of iodide of silver in nitrate of silver is of importance in the determination of iodine, as this may be rendered less exact by the presence of any considerable excess of nitrate of silver.—*Liebig's Annalen*, xcv. p. 127.

ANALYTICAL CHEMISTRY.

On the Volumetric Determination of the Iodides in the Presence of Metallic Chlorides and Bromides. By A. and F. DUPRÉ.

At the recommendation of Bunsen, the authors have endeavoured to find a method for the volumetric determination of iodine in cases where bromine or chlorine is present with the iodine. As iodine can be very exactly determined by Bunsen's method, iodides can be decomposed by chlorine or bromine, and then the iodine is determinable by the following process, even in the presence of these two similar bodies.

The process is founded upon the circumstance that chlorine first of all separates iodine from an iodide, and then, if the quantity of

* See Chem. Gaz., Sept. 15, 1855, p. 347.

chlorine be sufficient, converts it into ICl^5 , and afterwards into ICl^3 . The latter compound is destitute of the property of giving a dark violet colour to chloroform and sulphuret of carbon, which is possessed by iodine and chloride of iodine, ICl . If therefore the solution of a metallic iodide, which has been gradually more and more chlorinated, be shaken with sulphuret of carbon, the latter is constantly acquiring a stronger violet colour, until at last, at the moment when all the iodine is converted into ICl^3 , the colour disappears. This point occurs suddenly and with the greatest distinctness.

The execution of this process requires in the first place a fluid containing chlorine, the amount of chlorine in which is known for each degree of the burette. It is prepared by adding chlorine water to a litre of water, and then ascertaining the strength by Bunsen's method. The amount of chlorine contained in one degree of the burette of this fluid = C . The fluid to be tested for iodine is put into a stoppered glass with a few grammes of sulphuret of carbon or chloroform, the standard solution of chlorine is added to it, and the whole shaken strongly at every addition, until at last the violet colour of the chloroform or sulphuret of carbon disappears; then if T degrees of the burette have been added, the quantity of chlorine employed = TC . This quantity has consequently served to displace the iodine in the compound, and at the same time to convert it into ICl^5 . 1 equiv. of iodine is therefore converted into ICl^5 by 6 equivs. of chlorine. If therefore x be the quantity of iodine to be determined, we have

$$\text{I. } x = \frac{T \cdot C \cdot J}{6Cl}.$$

When this method is employed, oxides and organic substances, which are decomposed by chlorine or iodine, must of course be absent. If such substances be present, the fluid is mixed with solution of chlorine of undetermined strength, until the violet colour of the sulphuret of carbon serving as the index disappears. At this period the iodine is therefore present as ICl^5 . If a solution of iodide of potassium be then added, exactly 6 atoms of iodine will be set free for every atom of ICl^5 . This free iodine is determined by the usual method, and the quantity found divided by 6.

If the fluids in which iodine is to be determined contain bromine, the following observations upon the behaviour of bromine towards iodine are to be taken into consideration.

Solution of bromine first of all separates free iodine from the solution of a metallic bromide or iodide, and this gives a violet colour to sulphuret of carbon. If the amount of the metallic bromide be so great that more than 1 part of bromine occurs in 2500 parts of water, bromide of iodine, BrI , is formed. At the time of the formation of this compound, the sulphuret of carbon has the yellowish-brown colour of zircon. To establish a method of determining the iodine in iodides upon this property, 1 part of bromide of potassium is added to 1500 parts of the solution of the metallic iodide; the process in other respects is the same as before, and either solu-

tion of chlorine or of bromine may be employed. The quantity of bromide of potassium is to be increased when testing with solution of chlorine, the greater the quantity of iodine in the solution under examination. As in this case, however, instead of 6, only 2 atoms of chlorine are employed for 1 atom of bromine separated, the above formula for x is changed to,—

$$\text{II. } x' = \frac{\text{T} \cdot \text{C} \cdot \text{J}}{2\text{Cl}}.$$

The following process however is much better; it is founded upon the behaviour of iodine with bromine in much more dilute solutions. Thus if a solution contains less than 1 part of bromide of potassium to 1500 parts of water, higher compounds of bromine and iodine are formed together with IBr. If the solution be diluted with about 13,000 parts of water to 1 part of the metallic bromide, only the pentabromide of iodine, IBr⁵, is formed; and therewith the same distinct reaction again occurs, of the complete decoloration of the sulphuret of carbon or chloroform. All that is necessary therefore is to dilute the solution of the iodide containing a bromide so far with water, as that on the employment of solution of chlorine the transition from the rose-coloured to the colourless state may be clearly produced, and then to calculate with the above formula I.—Liebig's *Annalen*, xciv. p. 365.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Hydraulic Limes, Artificial Stones, and various new applications of the soluble Alkaline Silicates. (Second paper*.) By F. KUHLMANN.

Siliceous Paintings.—In his previous researches the author found that lime separated alumina from aluminate of potash, oxide of tin from stannate of potash, oxide of zinc from zincate of ammonia, and oxide of copper from cuprate of ammonia. He also obtained, with quicklime, and solutions of sulphate of alumina and other metallic sulphates, compounds which he has now formed by heating these solutions with carbonate of lime and other carbonates. He has also found that carbonate of lime removed the silica from solutions of alkaline silicates.

In 1841 he had found, that whenever a salt considered to be insoluble in water is brought into contact with a solution of a salt, the acid of which can form a still more insoluble salt with the base of the former, a transfer takes place; but this transfer is usually only partial, which leads one to suppose the formation of double salts.

By applying this law, he has succeeded in some degree in silica-

* See Chem. Gaz., No. 307, August 1, 1855, p. 298.

tizing carbonate of lead, chromate of lead, chromate of lime, and most of the metallic carbonates. From these researches he was led to the application of the alkaline silicates in painting. After referring to the use made in this way by Fuchs, Kaulbach, and Dingler of the alkaline silicates, he proceeds to give the following description of his experiments.

Painting on Stone.—These experiments were made with the view of employing concentrated solutions of silicate of potash, in place of oils, as a medium for laying colours on stone.

When white lead or oxide of zinc is triturated with a solution of silicate of potash, these substances are converted into silicate at the moment of contact, so that there is no time to apply the colour by the brush before it is consolidated. To render these colours fit for siliceous painting, this consolidation should be retarded by the addition of a considerable quantity of artificial sulphate of baryta, upon which the siliceous solution only exerts a slow action. The employment of sulphate of baryta alone gives great facility in painting, but this substance furnishes a semi-transparent tint with but little body. The artificial sulphate of baryta is a most important agent in paintings of this kind; it is a cheap white base, which greatly facilitates the application of colours in general.

Analogous results are obtained with different mineral colours. Some dry too readily, others too slowly, according to the intimacy and rapidity of the combinations between the coloured base and the silicic acid. These combinations usually retain a certain quantity of potash with great obstinacy. The colours which have succeeded best are vermilion, blue and green ultramarine, sulphuret of cadmium, the oxides of manganese, the ochres, oxide of chrome, &c. The colours which do not dry readily are fitted for painting by the addition of drying colours or whites.

When the colour is triturated with the siliceous solution, the paintings are executed with greater clearness upon silicatized stones, those which are not silicatized impoverishing the colour by absorption. The stones should at least be wetted once with a weak siliceous solution. When the paintings are to be cheaply done and not to be pumiced, the walls may be painted with colours ground with water, as in fresco-painting, and silicatized afterwards. This silicization may be effected by pumping the water through a fine rose from a small engine or large syringe.

Painting on Wood.—The difficulties in painting on wood arise from the circumstance, that instead of affording an unchangeable surface like stone, wood, by the action of the water which serves as the vehicle of the colour, warps to such an extent that some woods can scarcely receive adherent colours. The mere contact of the alkaline solution generally renders wood brown; thus young oak passes to the tint of old oak. The woods which most readily receive siliceous paintings are those with a white and close tissue, such as ash and wych-elm. Another inconvenience is, that when the colours and the siliceous coat which acts as a varnish are too thick, the painting scales off; but this also applies to ordinary paintings.

Painting on Metals, Glass, Porcelain, &c.—Siliceous paintings adhere firmly to metals if they be carefully kept from contact with water for some time; this is also the case with paintings on glass and porcelain. In painting on glass, the siliceous colours acquire a semi-transparency, which will allow of their employment in painted windows, and their low price may render it available in the decoration of houses.

Artificial sulphate of baryta, applied to glass by means of silicate of potash, gives a milk-white colour of great beauty; the sulphate is so intimately combined with the silica, that after a few days the silicate of potash is no longer removed even by washing with hot water. When glass thus painted is exposed to a high temperature, a fine white enamel is produced on its surface, which may economically replace the enamels with oxide of tin. Blue ultramarine, oxide of chrome, and pulverized enamels are of great value in this new mode of painting. If there is no chemical combination in all these applications of colour, there is at least a very strong adherence, caused by the siliceous cement, the hardening of which is no doubt facilitated by the excessively divided state in which it is exposed to the action of the air. Emery, oligistic iron, and especially peroxide of manganese, mixed in the state of very fine powder with concentrated solution of silicate of potash, form cements which acquire extreme hardness, and resist the action of heat without injury; they have however the disadvantage of not becoming completely insoluble in water for a long time. The cement of peroxide of manganese applied in thin layers upon the surface of iron, becomes vitrified by exposure to a high temperature.

Printing on Paper, Stuffs, &c.; Typography, Writing-ink.—The author has completely succeeded in the application of the siliceous solution to these purposes. The processes employed differ very little from those already in use. The most important condition to be realized is the maintenance of the siliceous colours in a constantly uniform state of humidity during their application. All the colours above referred to may be used in printing on paper and stuffs; printing in colours, and the application of gold and silver in leaves or in powder, are executed with facility, but care must be taken for certain colours to get rid of sulphurets in the preparation of the silicates. Silicate of potash enables us to fix ultramarine upon stuffs with more solidity and economy than by the processes now in use.

By triturating the finely-divided charcoal employed in the manufacture of Indian ink with a solution of silicate of potash, a writing-ink is obtained, which is almost indestructible by chemical agents. An analogous ink may be obtained by heating leather with caustic potash (Braconnot's ink), and adding gelatinous silica to the black carbonaceous matter thus produced, so as to saturate the potash. A decoction of cochineal mixed with a solution of silicate of potash furnishes a red ink, the colour of which long resists the action of chlorine and acids.—*Comptes Rendus*, August 6, 1855, p. 162.

THE CHEMICAL GAZETTE.

No. CCCXII.—October 15, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Contributions towards the Knowledge of Propionic and Butyracetic Acids. By H. LIMPRICHT and VON USLAR.

THE authors were induced to undertake the investigation, the results of which are here given, from the discrepancies found on the comparison of the statements made, on the one hand, regarding butyracetic acid, first described by Nöllner (1841), and afterwards more closely investigated by Nicklès, and on the other, with respect to propionic acid, with which the former has generally been regarded as identical. Strecker has declared the butyracetates to be double salts of propionic and acetic acids.

The authors obtained a considerable quantity of material from Prof. Wöhler, which had been procured from Nöllner himself. They have compared its salts with those of propionic acid. They first prepared propionic acid by decomposing cyanide of æthyle with alcoholic solution of potash. The acid thus obtained boiled constantly at 287°·6 F.

The Anhydride of Propionic Acid, $C^{12}H^{10}O^6$, was obtained by treating 1 equiv. of oxychloride of phosphorus with 6 equivs. of dry propionate of soda. It is a colourless fluid, not miscible with water, and possesses a disagreeable odour, resembling that of Valerian-root. It boils at 329° F. Analysis:—

C	55·01	12 =	72	55·38
H	8·00	10	10	7·69
O	..	6.	48	36·93

Propionic Æther, $C^{10}H^{10}O^4$, was obtained by the distillation of propionate of soda with alcohol and sulphuric acid. It is lighter than water, and smells like rum. It boils at 214° F. Analysis:—

C	59·20	10 =	60	58·82
H	10·41	10	10	9·80
O	..	4	32	31·38

Butyracetic Acid, $C^8H^6O^4$.—The lime-salt prepared by Nöllner was converted into the soda-salt, and this was distilled with sulphuric acid. The acid, which was obtained in large quantity, scarcely smelt like butyric acid, but rather like propionic acid; it is miscible with water in certain proportions, but does not mix with solution of chloride of calcium, and is not decomposed by this into acetic and butyric acids. It began to boil at 248° F., but the boiling-point

rose to 284° F., and without remaining stationary at this point, to 320° F. Propionic acid boils at $287^{\circ}6$ F. (Dumas). By frequently repeated fractional distillation, this acid was decomposed into butyric and acetic acids. The acid was also decomposed, forming the corresponding æthers, in the attempt to prepare the æther of butyric-acetic acid. Nor could the anhydride of the acid or the chloride of the double radical be procured; the corresponding compounds of the individual radicals were obtained.

Propione, Propylal and Propylene.—Dry propionate of baryta was distilled, and the gases evolved conducted first into receivers cooled with snow, and those which were not condensed in these, into a tubulated retort containing a mixture of chlorine. The greater part of the gas was condensed in the cooled receivers. The fluid here collected (1) consisted essentially of propylal and propione. In the chlorine mixture the chlorides of these bodies and of propylene or tritylene (2) were found. By the fractional distillation of the first of these (1),

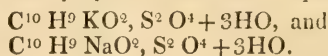
Propylal, $C^6H^6O^2$, was obtained; it stands in the same relation to the isomeric propylaldehyde as butyrol and valeral to butyraldehyde and valeraldehyde. It mixes with water, alcohol and æther, reduces ammoniacal solution of silver, and becomes yellow when heated with potash. Its ætherial solution, when saturated with ammonia, furnishes no crystals of propylammonia; in concentrated bisulphite of ammonia only a few verrucose crystals were formed. Its boiling-point appeared to be $150^{\circ}8$ F. Analysis gave:—

C	63.29	63.00	6 = 36	62.0
H	11.11	10.98	6 6	10.3
O	..	..	2 16	27.7

Propione, $C^{10}H^{10}O^2$, was obtained from the fluid by shaking the portion boiling between 203° and 248° F. with a concentrated solution of bisulphite of soda or potash, and distilling the crystals deposited with a solution of carbonate of potash. This body smells nearly like acetone. It boiled at 230° F., and consequently 18° higher than was found by Morley. Analysis gave:—

C	69.31	68.94	10 = 60	69.76
H	11.72	11.65	10 10	11.62
O	..	..	2 16	18.26

The Sulphites of Propione and Potassium or Sodium, from which the preceding body was prepared, have the composition,—



Both salts form nacreous scales. The corresponding ammoniacal salt is very soluble, and was not obtained in crystals.

Propylene or Tritylene, C^6H^6 .—This is also constantly formed during the distillation of the butyrate of baryta, but in such small quantity that only 1 grm. of protochloride of tritylene was obtained from 500 grms. The protochloride of tritylene, $C^6H^6Cl^2$, was obtained by the distillation of the bodies contained in the chlo-

rine mixture, together with the chlorides of the two preceding bodies; it passed over entirely below 248° F. By fractional distillation,—until it boiled at 219° – 230° F., and its vapour no longer produced tears which is the case with the chlorinated propylal and propione,—the protochloride of tritylene is obtained pure.

The *butyrate of baryta* may be obtained in good crystals, and may serve for the recognition of this acid.

Nitrate of silver produces a white precipitate in solutions of the salts, which undergoes little change in the light, but cannot be recrystallized from hot water without blackening. The *potash-salt* cannot be brought to crystallize in any way; it is even readily soluble in absolute alcohol, and is not separated from this solution by æther. The *soda-salt* also does not crystallize from water or alcohol, but on the addition of æther to the alcoholic solution, it shoots into acicular crystals.

From these experiments it appears, that butyric acid is certainly distinct from propionic acid. The question as to whether it is a peculiar acid, $C^6 H^6 O^4$, which is decomposed according to the equation $2C^6 H^6 O^4 = C^8 H^8 O^4 + C^4 H^4 O^4$, forming butyric and acetic acids, or only a mixture of these two acids, is left by the authors for the future to decide, as the facts contained in the foregoing paper are partly in favour of one view and partly of the other.—Liebig's *Annalen*, xciv. p. 321.

On Nitroglycerine or Glonoine. By J. E. DE VRIJ.

Nitroglycerine was first employed in medicine in America, under the name of glonoine. The author, who repeatedly paid attention to this body since its discovery by Sobrero, gives the following prescription for its preparation, which he has found most successful. 100 grms. of glycerine, of spec. grav. 1.262, dried at 302° F., are poured gradually into 200 cub. centims. of monohydrated nitric acid, which is to be cooled to 14° F. by a freezing mixture; care must be taken that the mixture does not become heated above 32° F. As soon as the two bodies have united into a homogeneous fluid, 200 cub. centims. of concentrated sulphuric acid are added in small quantities. If the temperature be constantly kept below 32° F., there is no danger of the mass going off in vapour, but this readily takes place if it rises above this point. The nitroglycerine then separates in the form of an oily stratum upon the acids, from which it is separated by means of a funnel furnished with a cock.

The weight of the quantity obtained was 200 grms. By mixing the separated acids with water, 20 grms. more were obtained. This whole quantity of 220 grms. was dissolved in as little æther as possible, and the solution was agitated repeatedly with fresh water until this no longer reddened litmus-paper; it was then evaporated on the water-bath, and the product was dried until its weight became constant. It then weighed 184 grms.

From this it appears that the constitution of nitroglycerine is $C^6 H^6 (NO^4)^2 O^6$; thus $C^6 H^6 O^6 = 92$ and $C^6 H^6 (NO^4)^2 O^6 = 182$.

It is a pale yellow oleaginous fluid, of spec. grav. 1.595 to 1.600 at 59° F. When heated to 320°, it is decomposed; this takes place with a strong explosion at a higher temperature. It also explodes when struck with a hammer upon an anvil. Sulphuretted hydrogen reacts upon it, with deposition of much sulphur.—*Journ. de Pharm. et de Chim.*, 3 ser. xxviii. p. 38.

On the Use of Hypochlorite of Magnesia and Hydrate of Magnesia as an Antidote in Poisoning by Phosphorus. By L. HOFMANN.

The author has made some experiments upon the action of hypochlorite of magnesia as an antidote against phosphorus; he has obtained results which contradict those of Bechert. Schrader also failed in saving rabbits poisoned with phosphoric acid by the employment of this agent. The author has repeated his experiments several times; equal quantities of the same food were given regularly during the last eight days to eight rabbits.

I. 1 gr. of phosphorus dissolved in poppy-oil was introduced into the œsophagus. In two minutes the symptoms of poisoning were manifested. The animal swelled up strongly and began to tremble; the head was bent back, the heart beat more frequently and more strongly, the creature began to groan, and in forty-six minutes death took place with convulsions.

II. The same quantity of granulated phosphorus, made into a pill with flour and water, was administered. The same phenomena took place as in No. I., but less rapidly. Death in two hours.

III. The animal received 1 gr. of phosphorus dissolved in poppy-oil; and as soon as the first symptoms of poisoning were manifested, the antidote was administered at intervals of a quarter of an hour, in doses of ℥ij. It was prepared with calcined magnesia ʒβ, solution of chlorine ʒβ, and distilled water ʒiijβ. The phenomena were as in No. I. Death occurred with convulsions at the administration of the seventh dose.

IV. The phosphorus was administered as in No. II., and the antidote was given immediately afterwards, and continued as in No. III. The same symptoms occurred, and death ensued in two hours twenty-five minutes.

The animals I. and II. were dissected immediately after death, III. and IV. twelve hours afterwards. No trace of corrosion was found in the stomach of the animals poisoned with dissolved phosphorus, but in those to which granulated phosphorus was administered the fundus of the stomach and the pylorus exhibited some rather strongly reddened spots. The right ventricle was greatly distended with coagulated blood, and both here and in the cerebral cavity the peculiar odour of phosphorus was distinctly perceptible.

These experiments prove that 1 gr. of phosphorus is sufficient to cause the death of a rabbit, and that phosphorus produces this effect far more rapidly when dissolved than when employed in substance.—*Archiv der Pharm.*, cxxxiii. p. 146.

On the Action of Glucose on the Salts of Copper in the Presence of Acetates. By M. ALVARO REYNOSO.

Sulphate of Copper.—It is well known that when sulphate of copper is boiled for a long time with glucose, it is decomposed, and metallic copper is precipitated. If the sulphate of copper be mixed with acetate of soda, potash, lime, magnesia, zinc, cobalt, nickel or manganese, and then boiled with glucose, a reduction is immediately produced, and protoxide of copper is precipitated. This reaction shows that sulphate of copper is decomposed by contact with these acetates, forming acetate of copper, which is reduced by the glucose.

Nitrate of Copper.—This salt, mixed with any of the above acetates, or with acetate of cadmium, strontian or lead, and boiled with glucose, furnishes a precipitate of protoxide of copper. Although this precipitate is also produced by boiling nitrate of copper alone with glucose, there is no reason to doubt the formation by double decomposition of acetate of copper, for in the latter case the reaction takes place at the moment of ebullition, whilst with the nitrate alone it requires long boiling.

Bichloride of Copper.—When concentrated solutions of bichloride of copper and acetate of soda are mixed, the acetate of copper soon crystallizes. At first sight it might therefore be supposed that the acetate of copper would remain in the mixture when boiled; but it is found by experiment, that at the temperature of ebullition the mixture is composed of bichloride of copper and acetate of soda; so that heat causes a reaction the reverse of that which takes place at ordinary temperatures. To see this phænomenon clearly, certain precautions must be taken. When bichloride of copper in excess is mixed with acetate of soda, a precipitate is formed, especially by boiling, which prevents the action of glucose on the mixture. The same precipitate is formed by mixing acetate of potash, magnesia, manganese, zinc, cadmium, strontian, cobalt, or nickel with the bichloride of copper. This precipitate is also produced by boiling acetate of copper with an excess of bichloride of copper, and also when chloride of sodium is added to acetate of copper.

If an excess of a very concentrated solution of acetate of soda be poured into a concentrated solution of bichloride of copper, and glucose be added to the mixture, protochloride of copper is formed on boiling, and its presence is more or less distinct according to the quantity of the acetate. If this be not in very great excess, the protochloride is seen to precipitate, leaving a colourless supernatant fluid. If the acetate of soda be in very great excess, the protochloride of copper is decomposed by it as fast as it is formed, and the final result is protoxide of copper.

Acetate of Copper.—When acetate of copper is boiled with glucose, whatever may be the excess of sugar and the period during which the mixture is boiled, the whole of the copper is never precipitated, some of it always remaining in the liquid. To effect the complete reduction of acetate of copper, it is sufficient to mix a great excess of acetate of soda or potash with this salt. This ex-

plains why the whole of the copper is precipitated when a great excess of acetate of soda or potash is mixed with the sulphate or nitrate of copper before boiling it with glucose.

Sesquisulphate and Sesquinitrate of Iron.—Acetate of copper, mixed with either of these salts, loses the faculty of being reduced by glucose. This character, and the peculiar colour of acetate of iron which makes its appearance at the moment of mixture, prove that the acetate of copper is decomposed by the iron-salts.

When acetate of soda is mixed with sulphate or nitrate of copper, acetate of copper soon crystallizes out.—*Comptes Rendus*, August 13, 1855, p. 278.

On Glucinum and its Compounds. By H. DEBRAY.

According to the author, glucinum is to be placed beside aluminium. It undergoes no change in the air even when heated. It does not decompose water at a white heat. It is not attacked by sulphur, sulphuretted hydrogen, and the alkaline sulphurets. Concentrated nitric acid does not attack it in the cold, and acts upon it with difficulty when heated. It is readily soluble in muriatic acid and in dilute sulphuric acid.

The *Oxide of Glucinum* does not approach so closely to alumina as Berzelius placed it. The most essential differences by which glucina is distinguished from alumina are as follows:—

Dry glucina absorbs carbonic acid from the air, and becomes converted into carbonate; and there exists a well-crystallized bicarbonate, and a double carbonate of ammonia and glucina, which do not occur with alumina.

Glucina is volatilized at a higher temperature without previous fusion, whilst alumina fuses before volatilization. Glucina rather resembles magnesia.

Chloride of Glucinum is less volatile than chloride of aluminium, so that by means of chlorine these two earths may be separated from one another in emery. Chloride of glucinum therefore rather resembles protochloride of iron. It is about equally volatile with chloride of zinc. Chloride of glucinum does not form with the alkaline protochlorides any double chlorides corresponding to spinelle, which, on the contrary, is the case with chloride of aluminium.

If we compare the formulæ of the salts of glucinum proposed by Berzelius and Awdejew,—

Berzelius.	Awdejew.
$3\text{SO}^3, \text{Be}^2 \text{O}^3 + 3\text{SO}^3 \text{KO} \}$	$\text{SO}^3 \text{BeO} + \text{SO}^3 \text{KO}$
$\text{Fe}^3 \text{Be}^2 + 3\text{FIK} \}$	$\text{FeBe} + \text{FIK}$
$3\text{C}^2 \text{O}^3, \text{Be}^2 \text{O}^3 + 3\text{C}^2 \text{O}^3 \text{KO}$	$\text{C}^2 \text{O}^3, \text{BeO} + \text{C}^2 \text{O}^3 \text{KO}$
$3\text{C}^2 \text{O}^3, \text{Be}^2 \text{O}^3 + 3\text{C}^2 \text{O}^3 \text{NH}^4 \text{O}$	$\text{C}^2 \text{O}^3, \text{BeO} + \text{C}^2 \text{O}^3 \text{NH}^4 \text{O}$
$9\text{CO}^2, 4\text{Be}^2 \text{O}^3 9(\text{CO}^2 \text{NH}^4 \text{O})$	$3\text{CO}^2, 4\text{BeO} + 3\text{CO}^2 \text{NH}^4 \text{O}$
+ 3HO	+ HO,

the latter certainly deserve consideration on account of their simplicity. But beyond this simplicity we find in the known salts no

further certain data, for glucina is not isomorphous with magnesia and lime.

Cymophane, which may be represented by the formula of spinelle, Al^2O^3 , BeO , differs so completely in its crystalline form from this class of bodies, that it cannot be united with the spinelles.

The author's conclusions are, that glucina should be regarded for the present as an earth which has no analogue. In its properties it stands just between the bases RO and R^2O^3 .—*Ann. de Chim. et de Phys.*, 3 sér. xlv. p. 5.

On Tartrate of Lime and a Reaction of Tartaric Acid.

By ARTHUR CASSELMANN.

The author, when occupied in the examination of Alexandrian senna, found that the aqueous extract deposited the lime-salt of an organic acid on evaporation. This salt possessed a remarkable property; when gradually heated, after the addition of ammonia and nitrate of silver, it covered the sides of the test-glass with a metallic speculum of silver, in such a manner that the reaction may be compared with the reduction of nitrate of silver by aldehyde-ammonia. Even a very small quantity of the lime-salt was sufficient to reduce the nitrate of silver in the manner above-mentioned, but only when the nitrate was added in small fragments, instead of in solution. If it were added in solution, the reduced silver was deposited in the form of a gray powder.

When the hot solution of the lime-salt was mixed with neutral acetate of lead, an abundant white precipitate was obtained, which however always contained traces of the lime-salt, unless the fluid was rapidly filtered whilst boiling. This precipitate was decomposed by sulphuretted hydrogen; the fluid containing the pure acid was evaporated, and the acid was obtained as a syrupy sharply-acid fluid, which exhibited no trace of crystallization even after standing for several weeks.

The author analysed the lead-salt of the acid; it had the composition of tartrate of lead. Analysis gave:—

C	13.5	8	= 48.0	13.5
H	1.5	4	4.0	1.1
O	22.7	10	80.0	22.6
PbO	62.3	2	223.2	62.8

Comparative experiments with artificially-prepared tartrate of lime presented the same behaviour. The remarkable fact, that tartaric acid, in one of its least soluble compounds, possesses the property of instantaneously reducing nitrate of silver, might be made use of in analysis for the detection of minute traces of this acid. Ræemic acid however gives the same reaction, and also produces it instantaneously only when the nitrate of silver is added in the solid state.

Tartrate of lime occurs in considerable quantity in senna-leaves; but, from its sparing solubility, is not obtained from them without

difficulty. The author has made experiments upon the solubility of tartrate of lime, and found that this salt requires for its solution 350 parts of boiling, and 1210 parts of cold water.

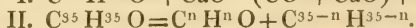
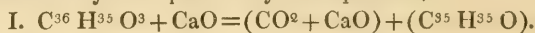
The author also boiled tartrate of silver with ammonia, to ascertain whether, as stated by Werther, a new ammoniacal salt is thus produced. He was unable to find anything of the kind.—*Archiv der Pharm.*, lxxxiii. p. 148.

Examination of the Products of Distillation of pure Stearate of Lime. By Prof. HEINTZ.

Bussy states that by this operation stearone is produced; a body, which may be regarded as anhydrous stearic acid from which so many equivalents of carbonic acid have been separated as it was capable of saturating of base. Rowney however has recently asserted that the solid fusible body formed is constituted according to the formula $C^{28}H^{28}O$. He calls it *stearene*.

From the results of the previous investigations of Heintz upon the products of the distillation of hydrated stearic acid, we may draw the conclusion, that Bussy's view of the products of decomposition of stearate of lime is the correct one, and that it only requires correction inasfar as the stearone formed is itself partially decomposed by the heat required for the decomposition.

The examination of the products of distillation of stearate of lime has shown that this conclusion is perfectly correct. The author found, in this operation, that the products were partly gaseous and partly solid. The former consist of hydrocarbons of the formula C^nH^n , and of light carburetted hydrogen, which is produced from the former by separation of carbon; the solid products consist of stearone ($C^{35}H^{35}O$), and other cetones, which are produced along with the hydrocarbons by the decomposition of the stearone. The decomposition may be expressed by the equations,—



The author obtained pure stearone by repeated extraction of the above-mentioned products of distillation with alcohol, and recrystallizing the undissolved portion from its solution in boiling æther. It possessed all the properties of that produced by the distillation of hydrated stearic acid, but its melting-point was a little higher, namely $189^{\circ}8$ F.; this is evidently from its greater purity.

To determine the atomic weight of stearone, the author prepared a product of substitution by means of bromine, which he found to be constituted according to the formula $C^{35} \left\{ \begin{smallmatrix} H^{34} \\ Br \end{smallmatrix} \right\} O$.

From the analysis of the portion of the crude stearone which was soluble in alcohol, it appeared that it contained the same number of equivalents of hydrogen and carbon, but a larger amount of oxygen, showing that it contained (perhaps together with stearone) other cetones with a smaller amount of carbon and hydrogen.—*Ber. der Akad. der Wiss. zu Berlin*, 1855, p. 385.

On the Behaviour of the different Bases towards Solutions of Ammoniacal Salts, and especially of Chloride of Ammonium. By H. ROSE.

The author has ascertained by a series of investigations, that there is no more certain means of ascertaining the strength or weakness of the basic properties of the different metallic oxides than treating them with solutions of inodorous ammoniacal salts, and especially of chloride of ammonium. All metallic bases of the atomic composition $2R + O$ and $R + O$ decompose solution of chloride of ammonium, producing evolution of ammonia, and dissolving if their chlorides be soluble in water. Even those bases which, although undoubtedly composed of $R + O$, belong to the series of weak bases, and can be separated from solutions of their salts at ordinary temperatures by carbonate of baryta, and sometimes even by water, are capable of decomposing chloride of ammonium when heated with its solution.

On the other hand, the bases of the composition $2R + 3O$, as well as those which contain more oxygen, are unable to decompose a solution of chloride of ammonium even when long boiled with it, so that the atomic constitution of the different oxides may be best determined by their behaviour towards this solution.

This apparently universal rule has only a single exception; glucina is capable of decomposing the solution of chloride of ammonium, and becoming dissolved. But of all the bases of the composition $2R + 3O$, this is undoubtedly the strongest, so that many chemists have attributed to it the composition $R + O$. It was only the agreement in the crystalline form of glucina which had been exposed to the heat of a porcelain furnace with that of alumina, and the corresponding atomic volumes of the two bases, that formerly determined the author to ascribe the composition $2Be + 3O$ to glucina. Moreover, it loses the property of decomposing chloride of ammonium when it has previously been strongly heated.—*Ber. der Akad. der Wiss. zu Berlin*, 1855, p. 333.

Note on the Reduction of Oxide of Zinc and the Alkalies.

By H. SAINTE-CLAIRE DEVILLE.

If we take, as I have often done, 10 or 15 grms. of pure oxide of zinc, introduce them by means of a tray into a porcelain tube of about 3 centims. in diameter, through which a current of pure hydrogen is passed not too quickly, and heat them gradually to a very high temperature, no reduction is produced; the oxide of zinc is merely displaced in the porcelain tube, and produces artificial *cadmies**, which form very distinct and often bulky crystals in the parts of the tube which are still hot. This experiment led me to disagree with the common opinion, that oxide of zinc is reducible

* A spurious sublimation of oxide of zinc, which takes place during the treatment of many ores containing zinc in the blast-furnace.—*Ed. Chem. Gaz.*

by hydrogen; and I attributed the difference to the absolute purity of the substances brought in contact*; we might also conclude that pure oxide of zinc is volatile in a current of hydrogen at a high temperature.

However, some peculiar circumstances in the manufacture of zinc communicated to me by M. Rivot, to whom we are indebted for some excellent papers on this subject, and some facts which I have myself observed in the preparation of another volatile metal, sodium, induced me to doubt the validity of the conclusions derived from the experiments to which I have just referred.

These experiments were therefore resumed at the same time at the Ecole des Mines, where M. Rivot obtained metallic zinc by means of pure oxide and hydrogen, and at the Ecole Normale, where I again obtained nothing but crystallized oxide of zinc. The comparison of the apparatus soon explained these contradictory facts; M. Rivot operated upon 5 grms. of oxide of zinc enclosed in a narrow tube, and the evolution of the hydrogen was incomparably more rapid than in my operations. It is the difference in the quickness of the hydrogen in the tube containing the oxide of zinc, that introduces a capital difference in the apparent results; with a rapid current metallic zinc is obtained, with a slow current nothing but crystallized oxide of zinc. It is evident that in the second case the water originally formed is entirely decomposed by the metallic vapours, and that the volatility of the oxide of zinc is in this case only apparent. We have also ascertained that it is decidedly not volatile when air is substituted for the hydrogen. This singular experiment on the transport of oxide of zinc in hydrogen, must therefore be interpreted in quite a different manner from that which I had originally supposed, and cannot serve as the basis of any explanation relative to the metallurgy of zinc, as I had at first hoped.

But there are some other consequences of the experiment to which I wish to call attention. In the first place I would observe, that what is called in chemical theories an action of *mass*, does not play any part in this case. On the contrary, at the moment when the vapours of water and zinc react to reproduce oxide of zinc and hydrogen, this gas predominating in the mixture, ought, by virtue of its mass, to protect a portion of the metal from oxidation. This never takes place when the operation is carried on with sufficient slowness. But everything is explained by admitting the reversal of the affinities by the variation of the temperatures; thus in the part of the tube which is directly heated, zinc and water may coexist in vapour, but in the cooler parts, where the cadmies are deposited, the affinities change, the water is decomposed, and every trace of metallic zinc disappears. This is what takes place in my experiments; but when the hydrogen passes rapidly, this zone of the tube in which the inverse reaction is effected, is traversed by the mixture of vapours with such rapidity, that the refrigeration of the materials pre-

* It is well known that absolutely pure metallic zinc is scarcely attacked by hydrated sulphuric acid.

vents the ulterior reaction. It is consequently a true *mechanical* action, which stands in the way of the normal development of the two phases of the experiment. Thus the exclusive production of cadmies is possible, whilst the protection of the metallic zinc against the action of the aqueous vapour is never complete, even in experiments in which all the most favourable conditions for complete reduction have been fulfilled; even then a small quantity of oxide of zinc is found deposited in the tube, beyond the points to which the heat is applied directly, but in the parts nearest to them, on either side of the tray*.

This influence of the mechanical action of the reductive gases is observed in a striking manner in the production of sodium, with which I am at present occupied in an economical point of view. I have been led to substitute coal for wood-charcoal, in the mixture of carbon, chalk and carbonate of soda, which serves for the preparation of this metal. The great improvement in the result must be explained by the influence which the greater quantity of gas evolved exerts upon the operation, an influence of the same kind as in the reduction of zinc. Oxide of carbon and sodium may coexist at a cherry-red heat, but at a dull red heat soda and carbon are formed; and in order to obtain as much sodium as possible, it is necessary only to cause the vapours to pass with the greatest rapidity, and to cool them as quickly as possible in those parts of the apparatus, whatever may be their form, where the dangerous temperature prevails.

The approximation which must be made in this case of sodium and zinc explains why I persist in ranging zinc next to magnesium in the series of metals, although oxide of zinc is reducible by hydrogen. It is probable that if magnesium were volatile, magnesia would be decomposable by charcoal, and perhaps by hydrogen; and the same will apply to calcium and the metals of the alkaline earths, in relation to the alkaline metals of which the oxides are reducible by charcoal. It appears to me that this property of metals, of being reduced with more or less facility, depending particularly upon one of the physical properties which has the least relation to their chemical affinities, should have little weight in their classification. Moreover, we know little of the different degrees of volatility of the metals of this kind, and even of the other metals at the highest temperatures. Thus I have reduced considerable quantities of platinum into condensable vapours by means of a forge fed with blocks of wood; and we may hope that some of the metals of the alkaline earths will not be more refractory than platinum. If this be the case, the mode of preparation of sodium would be applicable to them, viz. by increasing considerably the temperature and the rapidity of the currents of the reducing gases. The greatest diffi-

* By varying the rapidity of the current of hydrogen, the diameter of the vessels and the quantities of oxide of zinc, we may obtain sometimes cadmies, sometimes a mixture of oxide of zinc and metallic zinc, and sometimes metallic zinc with a very small quantity of oxide.

culty rests in selecting the vessels applicable to such experiments, and I hope that I have got rid of this.

I have published a method of analysis founded on the resistance of oxide of zinc to the reducing action of hydrogen at a temperature at which the oxides of copper, lead, iron, &c., are very easily reduced to the metallic state. All my verifications were made on the supposition that oxide of zinc itself is capable of being reduced, but at a much higher temperature, which is undoubtedly the case; and they have decidedly convinced me, that, at the heat produced by a Berzelius lamp, oxide of zinc enclosed in a glass tube does not lose the least portion of its weight in contact with hydrogen, which furnishes a limit of the resistance of oxide of zinc to reduction by hydrogen.—*Ann. de Chim. et de Phys.*, April 1855, xliii. p. 477.

On the Coloration of Glass by the Alkaline Sulphurets, and its Changes of Colour, analogous to those of Sulphur when heated.
By D. C. SPLITGERBER.

In the year 1839, I drew attention to a yellow glass, whose remarkable properties have obtained a new explanation from the interesting researches of Magnus upon red and black sulphur, as it appears as though the sulphur possessed these modifications even in its combinations with the alkaline metals, to which the silicates owe their colour.

To render what follows more intelligible, I shall briefly repeat something from my preceding communication, and observe that this glass is obtained by mixing a carbonizable substance, such as bark, tartar, sugar, &c., with the ordinary materials of white glass, leaving out however all additions capable of giving off oxygen.

It was consequently supposed formerly that this coloration was produced by carbon; but I showed that the yellow colour was caused by sulphur, or rather by its combination with the alkaline metals, which had been reduced by the carbonaceous addition from the sulphates by which the potash or soda employed had been contaminated; these possess great power of communicating colour.

This glass, when it is of a sufficiently deep colour, and appears brownish-yellow with a thickness of 4 millims., becomes gradually darker and less transparent when kept at a slight red heat, at which it does not soften, for about ten or fifteen minutes; but until it has become quite opaque, it only allows the simple red light to pass, and furnishes the so-called black glass, which is employed in polarizing apparatus, and which, when of the proper degree of transparency, is also very fit for the observation of the sun, which is thereby deprived of its brilliancy.

If this glass, which has become as opaque as possible (the exact hitting of this point requires some practice), and which during its first heating has retained its sharp edges, be exposed to a higher temperature, so that the edges become rounded and the surfaces bowed, it regains its transparency, and again exhibits its original colour; if re-heated a little, it again becomes darker.

The process by which this remarkable change of colour in the glass is produced, in which a chemical decomposition of the different constituents cannot be admitted, is, that at a slightly elevated temperature the metallic sulphuret passes into the modifications analogous first to the red, and afterwards to the black sulphur, separating in the latter state, so as at last to render the glass quite opaque, at least if the metallic sulphuret be present in sufficient quantity, for a pale yellow glass does not become dark, far less opaque, when heated. But at the commencement of the fusion of the glass, the black metallic sulphuret is again dissolved by the mass, and reconverted into its previous condition of the yellow modification.

On analysis, I found that a brownish-yellow glass of this kind, which beautifully showed the change of colour, consisted of,—

Silica	62·43
Lime	9·46
Alumina, oxides of iron and manganese. .	1·72
Potash	26·04
Sulphur	0·35

So that it contained about a third per cent. of sulphur, calculated from the sulphate of baryta which was thrown down by chloride of barium after the silica had been filtered off and crystals of nitrate of potash had been added to the fused red-hot mass in order to oxidize the sulphur. In the preparation of a glass of this kind, the addition of $1\frac{3}{4}$ per cent. of sulphate of soda together with sugar to the pure materials of white glass, gave a strong brownish-yellow colour; this glass therefore contained only about $\frac{1}{3}$ per cent. of sulphur.

On the addition of sugar alone to the pure materials, the glass remained white, as was to be expected, for the sugar burnt away without leaving any trace in the glass; however, it is possible that under peculiar circumstances, as for instance when the fusion is effected in a closed crucible, carbon may remain in the glass. I shall make experiments upon this subject.

As has been previously mentioned, the yellow glass in its different changes has the greatest similarity with heated sulphur; the coloured spectrum, when observed through it, loses all the more strongly refractive rays as the thickness and colour increase, until at last only the extreme red remains visible; whilst both substances in thinner strata allow orange, yellow, and a little green light to pass through besides the red. Smoked glass, on the contrary, allows the passage of more yellow than red rays.

There was no difference in the power of this glass to allow the passage of heat in any of its modifications, when they were all of the same thickness; but, on the other hand, I found that white plate glass allowed the passage of more rays of heat, and that when the needle of the galvanometer was deviated 4° in the former case, it marked 6° in the latter; these two numbers, in this slight deviation, may be taken as the proportion of the rays of heat allowed to pass.

I have also endeavoured to form a photometer, although not quite

an exact one, for red light, with a plate of this dark red glass, by having it ground into a prism with a refringent angle of 4° . Upon this slides a metal plate furnished with an aperture, through which the different luminous bodies are to be observed; by means of divisions on the margin, the thickness of the glass may be calculated for the different places at which the object begins to be seen, and from this its intensity may be judged of. It is necessary however for this purpose that the glass plate should be uniformly coloured throughout, which is rarely the case. It would be better to cut the refringent angle less than 4° , and to slide two such prisms upon one another, so as to produce any thickness that might be required.—Poggendorff's *Annalen*, xcv. p. 472.

On a new Base, derived from Nitrocoumarine.

By A. FRAPOLLI and L. CHIOZZA.

In his examination of coumarine*, Bleibtreu mentions some experiments to effect the reduction of nitrocoumarine. The product obtained by this chemist by the treatment of an alcoholic solution of nitrocoumarine with sulphuret of ammonium was not crystallizable, and dissolved in ammonia; it gave precipitates containing sulphur with salts of lead and silver. The action of the commonly-employed agents of reduction also did not lead to simple and determinate results. Hydrogen in the nascent state, when evolved in a solution of nitrocoumarine in potash, has no action upon this body. The same is the case when hyposulphite of potash or ammonia is employed. The only process by which we succeeded in reducing nitrocoumarine was by the employment of protacetate of iron, a body the advantages of which in the reduction of similar nitro-compounds have been already pointed out by Béchamp.

If nitrocoumarine be treated with a mixture of dilute acetic acid and iron filings, an action soon commences, especially when the mixture is heated upon the water-bath. Peroxide of iron is separated abundantly, and on the cooling of the mixture, yellow needles are deposited upon the walls of the vessel. In order that the action may be complete, the substances should be left in contact for twenty-four hours. The precipitated peroxide of iron is then filtered from the solution of protacetate of iron. The solution is evaporated, and repeatedly filtered whilst hot during the evaporation, in order to separate the peroxide of iron formed during this process; and on cooling it furnishes yellow acicular crystals of a substance which has all the characters of an organic base, and which we call *coumaramine*.

When the precipitate is treated with alcohol, the latter takes up a further quantity of coumaramine, which is purified by evaporating the alcoholic solution on the water-bath, and redissolving the residue in water. This second aqueous solution is treated in the same way as the former one.

* Chem. Gaz., vol. iv. p. 267.

During the concentration of the aqueous solutions and their filtration, a portion of the coumaramine appears to undergo decomposition, and the crystals obtained from such solutions are always contaminated by an amorphous brown precipitate.

The crystals first separated were purified by recrystallization from water; they then formed beautiful prismatic needles, of a reddish-yellow colour. When a few grammes of the substance are operated with, crystals may easily be obtained of 6 to 8 centims. in length. These crystals are very slightly soluble in cold water; they appear to dissolve more readily in a saturated solution of protacetate of iron. Coumaramine dissolves readily in boiling water, and also in boiling alcohol. The saturated boiling alcoholic solution sets on cooling. Coumaramine is nearly insoluble in æther. It fuses between 344° and 348° F.; and when carefully heated to a higher temperature, gives off yellow vapours, which condense into pale yellow laminae. When heated rapidly in a glass tube over the spirit-lamp, it becomes brown, and distils over in the form of a heavy oil, which solidifies into yellow crystals; these are contaminated with a small portion of an oil which smells like aniline. The analysis of coumaramine gave,—

	Found.			Calculated.
	I.	II.	III.	
C	67.5	67.3	..	67.08
H	4.3	4.5	..	4.34
N	..	..	9.1	8.69

These numbers agree with the formula $C^9 H^7 NO^{2*}$.

Coumaramine combines readily with muriatic acid, forming a salt which is very soluble in water, and crystallizes in laminae. On adding ammonia to an aqueous solution of muriate of coumaramine, the fluid sets into a mass of crystals of coumaramine.

A boiling solution of caustic potash rapidly decomposes coumaramine. If the fluid be afterwards neutralized by an acid, brown flakes are obtained.

By the addition of a solution of chloride of platinum to a solution of muriate of coumaramine, a yellow crystalline precipitate, insoluble in water, is obtained. 0.192 of this double salt gave 0.052 of platinum, representing 26.7 per cent. The formula $C^9 H^7 NO^2, ClH, PtCl^2$ requires 26.9 per cent.—Liebig's *Annalen*, xcv. p. 252.

On a new Compound of Sulphocyanogen with Ætherine.

By F. L. SONNENSCHNEIN.

From the isomerism of metacetylene with allyle, and the garlic-like odour of the compound $C^4 H^3 Cl$ (chlorætheride, chloroparacetylene, protochloride of vinyle), prepared with an alcoholic solution of potash

* According to Gerhardt's notation; in the ordinary method, $C^{18} H^{17} NO^4$.

from chloride of ætherine, it might be supposed that this compound contained a radical homologous with allyle, $C^6 H^5$.

The author has therefore induced E. Meyer to study the products of metamorphosis of chloride of ætherine, $C^4 H^3 Cl + HCl$, by sulphocyanide of potassium. The author states that further experiments will be made upon the preparation of the bodies of the oil of mustard series.

An alcoholic solution of chlorine of ætherine was heated to $212^\circ F.$, in a sealed glass tube, with 1 equiv. of sulphocyanide of potassium. Chloride of potassium was formed, together with the new compound *bisulphocyanide of ætherine*, $C^4 H^4 + 2(C^2 NS^2)$ or $C^4 H^3 + C^2 NS^2 + HC^2 NS^2$. It is obtained from the residue in the retort after the fluid has been distilled off, by evaporation, and extraction of the chloride of potassium and the excess of sulphocyanide of potassium with water. The residue is purified by recrystallization.

Properties.—It forms beautiful crystals of a peculiar odour, intermediate between that of horse-radish and that of assa-fœtida; its taste is pungent, producing a burning sensation in the throat. On the skin it produces a violent itching, without forming blisters; and when heated, either by itself or with water, produces sneezing and tears. At $194^\circ F.$ it melts into an oil, which is heavier than water, and on cooling solidifies into a beautiful radiate mass, which has a shining fatty appearance. By careful heating on the oil-bath, a small portion is sublimed; the greater part is carbonized, with evolution of hydrocyanogen and ammoniacal and other products. It is soluble in alcohol and æther, and also in chloride of ætherine. Its alcoholic solution does not give the characteristic reactions of the sulphocyanides with salts of oxide of iron. It is decomposed by potash; the fluid immediately acquires a different odour, with the reaction of a sulphocyanide, and separates carbonate of potash. By boiling for a time with baryta-water, it deposits carbonate of baryta, and sulphocyanide of barium is formed. Freshly-precipitated hydrated oxide of lead is blackened by boiling with this compound, and the fluid is afterwards reddened by perchloride of iron; by the addition of potash, the blackening of the lead precipitate is more rapid. Acids do not separate sulphocyanogen. The alcoholic solution produces a white precipitate in a solution of perchloride of mercury. Ammonia does not immediately destroy the odour, but a white turbidity soon appears, and in the course of a few days a flocculent precipitate is produced; the solution then contains sulphocyanide of ammonium.

If the composition of chloride of ætherine be $C^4 H^3 Cl + HCl$, the new compound is evidently produced by simple decomposition; $C^4 H^3, CyS^2 + HCyS^2$, that is to say, chloride of ætherine in which the chlorine is replaced by sulphocyanogen.

From this it is probable that bodies homologous with oil of mustard may also be prepared. The alcoholic solution of the body $C^4 H^3 Cl$ also gave a fluid having a mustard-like odour with sulphocyanide of potassium.—*Journ. für Prakt. Chem.*, lxx. p. 257.

On the Preparation and Purification of Hippuric Acid and its Compound with Oxide of Zinc. By D. J. Löwe.

In order to obtain hippuric acid directly from the urine, the author mixes fresh urine with an excess of sulphate of zinc, and evaporates it, together with the precipitate of phosphate and basic carbonate of zinc produced by the addition of the zinc-salt, to one-sixth or one-eighth of the original volume. This is quickly filtered; the precipitate is washed on the filter with a little hot water, and the filtrate decomposed by means of dilute sulphuric or muriatic acid. After this operation, the entire fluid solidifies into a white jelly of hippuric acid, in a state of purity which is not obtained by any other known method. It is collected upon a filter, and washed with cold water as long as the drops passing are of a yellowish colour; it is afterwards dried by pressing between several folds of blotting-paper. By this process all that is necessary to obtain the acid in large crystals, is to recrystallize it. As it is not always possible to obtain large quantities of fresh urine, it is advisable, especially in the hot season, to pour it into tall vessels of stone-ware, into which a sufficient quantity of a solution of sulphate of zinc in water, or dilute muriatic acid, has been previously put.

To purify a coloured hippuric acid, we may avail ourselves of its behaviour towards metallic zinc, which is cut into small pieces, and boiled with the solution of the acid. The metal is strongly attacked, with evolution of hydrogen. The solution acquires a slight yellowish colour, and when the salt is completely formed, it solidifies on cooling into a thick crystalline jelly. If towards the close of the operation, when the metallic zinc is but faintly attacked, a little freshly-calcined animal charcoal be added to the boiling fluid, and this is then filtered and the filtrate allowed to run into dilute sulphuric or muriatic acid, the hippuric acid separates in beautiful white crystals. It is only when a considerable portion of the acid remains uncombined, that it still retains a slight yellowish colour after the precipitation.

When the quantity of acid to be purified is considerable, this operation is rather tedious, even when a small addition of an electro-negative metal (such as platinum or lead) has been made to the zinc. With large quantities the acid is dissolved in as little water as possible, and neutralized with carbonate of soda; to this solution a slight excess of pure sulphate of zinc is added, and it is then boiled for a short time with animal charcoal, and filtered into a dilute muriatic acid, by which the hippuric acid is separated in colourless crystals. A slight excess of carbonate of soda is not injurious; on the contrary, the basic carbonate of zinc separated on the addition of sulphate of zinc holds a portion of the colouring matter, and consequently facilitates the decolorization.

Hippurate of Zinc, which is formed on the addition of sulphate or chloridic of zinc to the solution of a hippurate, or by the boiling of metallic zinc with an aqueous solution of hippuric acid, has the formula $C^8H^5NO^3, ZnO + 5HO$. It is soluble in 53.16 parts of

water, and in 60.5 parts of alcohol of spec. grav. 0.82 at the temperature of 63° 5 F., and in 4 parts of boiling water. In boiling alcohol it dissolves still more readily. Cold and boiling æther scarcely dissolve it. At a high temperature it melts, and like free hippuric acid, when submitted to dry distillation, first acquires a red, and afterwards a black colour; and lastly, when long exposed to a red heat, it is completely decomposed, giving off aromatic vapours of nitrobenzole, and leaving ashes of oxide of zinc.—*Journ. für Prakt. Chem.*, lxx. p. 369.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Hydraulic Limes, Artificial Stones, and various new Applications of the Soluble Silicates. By M. F. KUHLMANN. (Third paper.)

Fixation of Potash in Siliceous Painting.—The application of paintings to calcareous stones by means of silicate of potash, enables us to explain how the colours may become entirely insoluble in water after being exposed to the air for some time. The contact of carbonate of lime with silicate of potash always causes the decomposition of this salt, and its sure conversion into silicate of lime, which retains the colouring matter, and even, according to the opinions lately put forward by M. Fuchs, the carbonic acid; but when the colours are applied to bodies which do not react upon the soluble silicate (such as wood, iron, glass, &c.), it becomes necessary to seek for the conditions of insolubility in the reaction of the colouring matter itself upon the silicate. With wood the difficulty may be got over by the previous application of a chalky coat of sufficient thickness to allow of pumicing; the chalk may be applied with size, or fixed with a very little of the silicate.

Even when the decomposition of the alkaline salts is produced by the colouring matter itself, there still remains a serious inconvenience, namely, the exudation of carbonate of potash in damp weather, until this salt is entirely got rid of. The author has found that washing the paintings with a weak solution of muriate of ammonia produces an absolute insolubility of the colour; but chloride of potassium remains, and this diminishes the brilliancy of the colours until it is completely got rid of by repeated washings.

Amongst the few chemical agents capable of consolidating potash, the only one that appeared to the author susceptible of employment in this case is hydrofluosilicic acid. By careful washing with this acid, the fixity of the colours was considerably increased, and

they were rendered completely insoluble. He considers this agent to be of the greatest utility in siliceous paintings of all kinds, but especially upon glass; it must be employed in a very weak solution, for when concentrated it possesses the remarkable property of dissolving most of the oxides.

Siliceous colours upon glass have a semitransparency, which it is important to preserve, but which gradually diminishes by the action of water. Glass painted with the silicate was boiled in water without the colours being detached; the colours were even brightened when viewed by reflected light, but when looked at by transmitted light they were sure to be dimmed, an effect which the author attributes to the state of opacity which they had acquired by the solution of a portion of the siliceous cement, which has the same effect upon these colours as oil upon paper. Careful application of hydrofluosilicic acid therefore gives a complete insolubility to paintings on glass, but, like muriate of ammonia, it slightly diminishes their transparency. It might perhaps be as well to give a slight varnish of pure silicate of potash at long intervals to paintings on glass exposed to the rain; but this can only be determined by long experience. The same varnish will also advantageously replace the essential oils in the application of certain colours upon glass and porcelain in the ordinary processes; it has not, like the essential oils, the defect of altering some colours by the reduction of the colouring oxides or salts.

Fluosilicization of Stones.—Although from his having kept stones treated with silicate of potash since 1841, without the appearance of any nitrification, the author considers treatment with silicate of potash* to be quite free from objections, he proposes the application of hydrofluosilicic acid to the treatment of stones, if only in case the silicate employed should have been too alkaline. After the hardening of the fat and porous limestones by their partial conversion into silicate of lime, he proposes to make sure of the insolubility of the potash retained in the stones, by impregnating them with a solution of hydrofluosilicic acid, gradually increased in strength, which penetrates the stone, and forms an insoluble compound with the potash. He thinks this process, which he calls *fluosilicization*, is of importance, as although the density acquired by the stone, and its impermeability to air and ammoniacal emanations, may prevent nitrification, the presence of potash must tend to give hygrometric properties to the walls, which may affect the healthiness of habitations.

The author next turned his attention to the direct employment of hydrofluosilicic acid in producing fluosilicization. This acid, when in contact with lime, is capable of dissolving a certain quantity of it without immediate precipitation of fluoride of calcium or separation of silica; but when it reaches a certain degree of satura-

* He observes that this may be done at the cost of one franc per square metre of surface.

tion, every fresh addition of lime completely decomposes the acid, removing all the solidifiable constituents so completely that no trace of them remains in the liquid. When carbonate of lime is substituted for quick-lime, the same effects are produced, and the silicium and fluorine penetrating the limestone, increase its hardness, but more slowly than when silicate of potash is employed. To diminish the corrosive action of the acid when first applied to the stones, and get rid of all danger of injury to the sculptures, the author proposes to saturate it partially with chalk, stopping at the moment when precipitation commences. This saturation should not be performed long before the employment of the liquid, as the acid gradually deposits a portion of the petrefactive principles which it contains.

The action of hydrofluosilicic acid upon plaster takes place almost instantaneously by simple contact in the cold, and the surface of the plaster is sensibly hardened; but if the injection of acid be abundant, the plaster is soon covered with rugose elevations, owing to the formation of a certain quantity of bisulphate of lime, the sulphuric acid not being capable of expulsion, like the carbonic acid of limestones.—*Comptes Rendus*, August 20, 1855, p. 289.

On the Preparation of Muriatic Acid, Sulphate of Soda, Nitric Acid and Chlorine, by the Employment of Sulphate of Magnesia in place of Sulphuric Acid. By M. RAMON DE LUNA.

The author has instituted some experiments, with the view of employing the native sulphate of magnesia, which occurs abundantly in several parts of Spain, in the preparation of several substances which have hitherto been prepared by means of sulphuric acid.

1. *Manufacture of Muriatic Acid and Sulphate of Soda.*—If a mixture of 1 part of chloride of sodium and 2 parts of crystallized sulphate of magnesia (or $1\frac{3}{4}$ of the dried salt) be heated to redness, muriatic acid is evolved, and the residue consists of sulphates of magnesia and soda. Water of 194° F. extracts the sulphate of soda from this residue; a little sulphate of magnesia is also dissolved, for which reason the solution is afterwards treated with milk of lime, in order to convert this salt into magnesia and sulphate of lime, and thus precipitate it. In this manner the author has prepared a quantity of 12,000 kilogrms. of sulphate of soda, which turned out to be purer than the ordinary salt.

2. *Manufacture of Nitric Acid.*—2 parts of crystallized, or $1\frac{3}{4}$ part of superficially-dried sulphate of magnesia, heated to redness with 1 part of nitrate of potash or soda, furnish nitric acid, with abundant nitrous fumes. 200 grms. of calcined nitrate of soda, heated with 400 grms. of crystallized sulphate of magnesia, furnished 90 grms. of nitric acid, of spec. grav. 1.38; by the distillation of this acid, a colourless nitric acid, of spec. grav. 1.46, was obtained.

3. *Chlorine.*—Chlorine may be obtained by heating strongly a mixture of chloride of sodium, oxide of manganese and crystallized sulphate of magnesia.—*Comptes Rendus*, xli. p. 95.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some of the Basic Constituents of Coal-Naphtha, and on Chrysène. By C. GREVILLE WILLIAMS, Assistant to Dr. Anderson, Glasgow University.

[Communicated by the Author, having been read at the Meeting of the British Association in Glasgow, September 13, 1855.]

THERE are few bodies of organic origin whose points of difference are more easily defined than the gelatinous tissues of bones, cinchonine, coal, and the bituminous shale of Dorsetshire; but a remarkable similarity is observed in the basic products of their destructive distillation, thus:—

Gelatinous tissues.	Cinchonine.	Coal.	Dorset shale.
Pyrrol*.	Pyrrol†.	Pyrrol§.	Pyrrol¶.
Pyridine*.	Pyridine†.	...	Pyridine**.
Picoline*.	Picoline†.	Picoline .	Picoline¶.
Lutidine*.	Lutidine†.	...	Lutidine¶.
Collidine*.	Collidine†.	...	Collidine¶.
...	Chinoline‡.	Chinoline§.	Parvoline¶.
Aniline*.	Lepidine†.	Aniline§.	

As soon as I had ascertained the nature of the basic products of the action of heat and alkalies on cinchonine, I could not fail to observe these resemblances, and I was anxious to ascertain whether the intervals which are seen to exist in the coal series, could not be filled up. Notwithstanding the numerous researches which have been made upon the substances alluded to, there are many points upon which our information is very scanty. Some of these are under investigation by abler hands, but there are others which I have promised myself to study. Among these may be mentioned the following:—1. Whether leukol and chinoline are really identical. 2. Whether pyridine, lutidine, and collidine, exist in coal-tar. 3. Whether lepidine or an isomeric base exists among the coal bases.

* Anderson, Trans. Royal Soc. Edinb., vol. xvi. part 4; vol. xx. part 2; and vol. xxi. part 1.

† Greville Williams, Trans. Royal Soc. Edinb., vol. xxi. part 2.

‡ Gerhardt, Revue Scientif. vol. x. p. 186.

§ Runge (1834), Poggendorff's Annalen, vols. xxxi. & xxxii.

|| Anderson, Trans. Royal Soc. Edinb., vol. xvi. part 2.

¶ Greville Williams (1854), Quart. Journ. Chem. Soc. Lond.

** Greville Williams (1854), Phil. Mag.

The first and last of these points are now under examination; the second forms the subject-matter of the present paper.

Before detailing the experiments, I should mention, in outline, the facts already elicited in the successive investigations of the coal bases, by Runge, Hofmann, and Anderson. The first chemist indicated the presence of kyanol and leukol (aniline and leukoline), but he did not attempt to ascertain their composition, which was done by Hofmann*, who extracted his bases from the less volatile portion of the distillate from coal-tar; and consequently did not meet with the pyridine series.

Dr. Anderson, in examining the fluid procured by agitating the ordinary naphthas with sulphuric acid in the process of purification, discovered picoline; but the quantity on which he worked was too small to enable him to find the other members of the series which were afterwards discovered by him in Dippel's oil.

During my investigation of the shale bases, I was induced to prepare a small quantity of those from coal, for the sake of comparison. I was not at that time able to procure access to the raw material, but by treating about one gallon of crude coal-naphtha in the manner described so often in the papers previously referred to, I procured about one and a half ounce of base, which, fractionated two or three times, gave about half that quantity of fluid, boiling at 270° Fahr. By treatment with nitric acid, to destroy the small quantity of aniline still remaining, and distillation with lime, I obtained the basic liquid in such a state, that when dry, a portion of it distilled over below 240° : it was still, however, far from pure, and the quantity was too small to allow of more than two or three fractionations; nevertheless, a platinum salt was obtained, giving on analysis the following numbers:—

	Experiment.	Theory.	
		Pyridine.	Picoline.
Carbon	22.1	21.0	24.1
Hydrogen	2.4	2.1	2.7
Platinum	34.1	34.6	32.9

It was evidently therefore a salt of pyridine, contaminated by a portion of the next base higher in the series.

Although this result pointed very unmistakeably to the presence of bases not generally believed to exist in coal-tar, I should not perhaps have returned for some time to the subject if it had not been, that, in consequence of my having ascertained the complex nature of the fluid which had hitherto been regarded in the light of pure chinoline, a fresh comparison of the latter in a pure state with leukol became necessary; and possessing, through the kindness of Mr. George Miller of Dalmarnock, the means of obtaining any quantity of coal-tar products, I availed myself of Dr. Anderson's permission to make use of his laboratory, and proceeded to examine, in the first place, the acid magma, produced by agitation of the crude naphthas with oil of vitriol. Nine gallons of the acid matter yielded (after

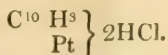
* *Annalen der Chemie und Pharmacie*, vol. xlvii.

separation of pyrrol and resins by protracted boiling, &c., as described in the previous papers) three quarts of crude bases, by far the greater portion of which boiled under 369° , although containing a large quantity of aniline. No leukol however appeared to be present. The basic liquid appeared therefore well adapted for determining the presence of pyridine, lutidine, and collidine.

The means of purification adopted were fractional distillation, treatment with nitric acid to remove aniline, and fractional crystallization of platinum salts, according to the methods described in my paper on the presence of pyridine among the shale bases, previously referred to. After several rectifications a portion was obtained boiling very steadily between 240° and 242° Fahr.; and as 240° was supposed to be the correct boiling-point of pyridine, a portion of the fraction was dissolved in hydrochloric acid and chloride of platinum added; fine prismatic crystals of a deep golden tint soon began to form; different preparations and crops obtained by evaporation of mother-liquors over sulphuric acid *in vacuo*, gave the annexed results on analysis:—

	I.	II.	III.	IV. & V.	Calculation.		
Carbon	..	..	..	21.05	21.03	C ¹⁰	60.0
Hydrogen	..	..	..	2.28	2.10	H ⁶	6.0
Nitrogen	..	..	..	..	4.93	N	14.0
Chlorine	..	..	..	..	37.34	Cl ³	106.5
Platinum	34.43	34.57	34.25	34.32	34.60	Pt	98.7

Although the analysis agrees perfectly with the theoretical numbers, and leaves no doubt of the identity of the base, I was desirous, if possible, of obtaining further proof, because small but perceptible differences are found in certain bases when obtained from different sources, although corresponding perfectly in boiling-point, composition, odour, and general characters. For the purpose required, no compound appeared more suitable than the very characteristic substance procured by prolonged boiling of the aqueous solution of the platinum salt of pyridine. When ebullition is continued for several days, the salt becomes converted into an insoluble powder, much resembling in appearance sublimed sulphur, and having, according to Dr. Anderson*, an analogous constitution to the bi-hydrochlorate of platinamine of Gerhardt. This view, it will be seen, supposes one equivalent of platinum to supply the place of two equivalents of hydrogen, the formula being,—



On boiling the platinum salt of pyridine from coal-naphtha for four days, a powder made its appearance, having all the physical properties of the substance sought. A platinum determination was all, therefore, that was considered necessary for its identification.

* Proceedings of Roy. Soc. Edinb., vol. iii.

3.195 grains of bi-hydrochlorate of platino-pyridine gave
1.260 platinum,

or, per cent.,

Experiment.
39.44

Theory.
39.68

As the crude coal-naphtha from which the raw material for the experiment was obtained had originally been distilled over in an atmosphere of steam at 212° Fahr., comparatively small quantities of the less volatile bases were present; some little labour was necessary, therefore, before the lutidine could be obtained in a sufficiently pure state for analysis. I was unable to procure the base itself quite free from picoline, as the quantity of material boiling as high as 310° was far too small to allow of the requisite number of fractionations. The portion distilling between 300° and 310°, after four rectifications, gave,—

Carbon.....	77.5	Theory. 78.5
Hydrogen	8.6	8.4

But, on converting the rest of the fraction into platinum salt, and fractionally crystallizing *in vacuo*, much nearer results were obtained. Several crops of platinum salt procured in this manner gave, on analysis,—

	I.	II.	III.	IV. & V.	Calculation.		
Carbon ..	..	..	..	26.81	26.81	C ¹⁴	84.0
Hydrogen ..	..	..	..	3.34	3.19	H ¹⁰	10.0
Nitrogen ..	..	..	..	..	4.49	N	14.0
Chlorine ..	..	..	..	..	34.00	Cl ³	106.5
Platinum	31.28	31.19	31.37	31.49	31.51	Pt	98.7

For convenience of comparison I place side by side the numbers obtained on analysis of platinum salts of lutidine from the various sources from which it has been obtained :—

	Dippel's oil. Dr. Anderson. (Mean.)	Shale-naphtha. Grev. Williams.	Cinchonine. Grev. Williams.	Coal-naphtha. Grev. Williams.
Carbon	26.35	26.14	26.94	26.81
Hydrogen	3.23	3.16	3.36	3.34
Nitrogen	..	..	..	..
Chlorine	..	..	..	..
Platinum	31.50	31.76	31.14	31.49

The next base (collidine) was present in such very small quantity that a great deal of time was occupied before it could be isolated; probably the three quarts of mixed bases did not contain more than three or four drachms. The amount operated on was much less than this (about three-fourths of a drachm); but with care a platinum salt was nevertheless obtained of considerable purity, for different crops gave on analysis,—

	I. & II.	III.	IV.	Calculation.		
Carbon	29.40	..	..	29.33	C ¹⁶	96.0
Hydrogen	3.83	..	..	3.65	H ¹²	12.0
Nitrogen	..	..	..	4.31	N	14.0
Chlorine	..	..	..	32.54	Cl ³	106.5
Platinum	30.07	30.02	30.16	30.16	Pt	98.7

I annex the results of analyses of the platinum salt of collidine from all the sources from which that base has been obtained except shale-naphtha; for in the latter case I was content with the result of the combustion of the base itself.

	Dippel's oil. Dr. Anderson.	Cinchonine. Grev. Williams.	Coal-naphtha. Grev. Williams.
	Mean.	Mean.	Mean.
Carbon.....	28.88	29.30	29.40
Hydrogen....	3.60	3.55	3.83
Nitrogen....	..	..	..
Chlorine....	..	..	..
Platinum....	30.08	29.99	30.08

With regard to parvoline, the next base of the series, it was impossible to obtain it in sufficient quantity for analysis without an expenditure of time altogether disproportioned to the importance of the result, and as I was sure of meeting with it in the examination, now in progress, of the bases in the dead oil, I was content to let that part of the inquiry remain for the present.

In examining the products which distil at a much higher temperature than dead oil, I was induced to make a few experiments upon the solid matter which is the last product obtainable by distillation from coal-tar. According to Laurent this is a mixture of chrysène and pyrène, and as according to Gerhardt the composition of the former is still doubtful, I repeated its analysis. The matter from which I procured it, and for which I am indebted to Mr. Kirkham of London, was in the form of a somewhat soft brilliant yellow mass, which had the property of darkening on exposure to light, becoming eventually of a brown tint. On digestion with æther, the greater part dissolves, leaving the substance sought in the form of a yellow powder, requiring prolonged washing with æther to remove the dark brown oily impurities which obstinately attach themselves to it. But even when the æther runs colourless, the chrysène is seen under the microscope to be contaminated by a small quantity of a black substance. This impurity was removed by dissolving the mixture in boiling Boghead naphtha, and filtering at a high temperature; the black matter remained on the filter, and, on the solution cooling, the chrysène crystallized out in a state of perfect purity, under the form of brilliant yellow spangles of great beauty. These were pulverized and well washed with æther to remove any adhering naphtha, and, after exposure to 212° until the weight became constant, the following result was obtained on combustion in a current of oxygen diluted with about its own bulk of atmospheric air:—

{	3·385	grains of chrysène gave
	11·745	... carbonic acid, and
	1·635	... water.

Experiment.		Calculation.		
Carbon . . .	94·63	94·74	C ¹²	72
Hydrogen. .	5·37	5·26	H ¹	4
	<u>100·00</u>	<u>100·00</u>		<u>76</u>

Laurent obtained—

	I.	II.
Carbon . . .	94·83	94·25
Hydrogen. .	5·44	5·30
	<u>100·27</u>	<u>99·55</u>

The empirical formula $n(C^{12}H^1)$ is therefore the correct expression of the ratio between the carbon and hydrogen; the value of n I hope eventually to ascertain by the action of reducing agents upon the nitro-compound, and as it may be a considerable time before I am able to renew the subject, I may mention that I found the nitro-compound, when pure, to be of a brilliant yellow instead of red as stated by Laurent. When dry it became excessively electrical, so much so, that, on endeavouring to remove it from the mortar, it flew in every direction. The small quantity of material at my disposal (only a few grains) was treated with sulphide of potassium, but I was unable to obtain an alkaloid by the usual means; perhaps in working on a larger scale I may yet succeed.

The quantity of pyrène present in the substance examined by me was so small that I was unable to obtain more than a few tenths of a grain.

It is evident, from the experiments detailed in the first part of this paper, that coal-tar contains members of at least three classes of homologous bases, namely, the pyridine, aniline, and leukoline series; for there can be no doubt that the latter is only one of a group; indeed, if leukol be really identical with chinoline, the fact of its being one of an homologous series is conclusively established by the existence of lepidine ($C^{20}H^9N$). Even if leukol is proved to be merely isomeric with chinoline, there is little doubt that it will not be found to exist alone; but this point I hope shortly to decide.

It is singular to observe the similarity which exists between the basic products from coal and cinchonine, the chief, perhaps almost the only, distinction of importance being the absence of aniline in the latter case; but if the nature of the substance decomposable by nitric acid existing in the less volatile fractions of the chinoline bases mentioned in the paper before adverted to, was properly understood, the parallelism would, perhaps, appear even closer than it does. Some experiments I have made, but which are not yet sufficiently advanced for publication, indicate that toluidine, or even still higher members of that class of alkaloids, are present among the basic products of the destructive distillation of certain nitrogenous bodies, and it is very far from improbable that in some cases where aniline

is absent, its place is supplied by one or more of its homologues. In fact it appears to me extremely doubtful whether aniline is the only member of the group to which it belongs present in coal-naphtha; this point is now under study.

In my paper on the volatile bases from shale-naphtha, I remarked, that although no evidence of the presence of aniline could be obtained, certain fractions gave with chloride of lime a brilliant green tint, and the apparently characteristic nature of the reaction induced me to apply to the substance giving the coloration a distinctive appellation. My result was also obtained by Dr. Anderson, under circumstances which appeared to preclude the possibility of error, I mean after destruction of the aniline present among the crude Dippel bases, by nitric acid, and recovery of the undecomposed alkaloids by distillation with lime. I have also obtained still more marked reactions of vertidine in operating on the crude bases from coal-tar. If a little solution of chloride of lime be added to some of the basic fluid mixed, by agitation, with water, the violet reaction of aniline becomes immediately manifest; but, at the same time, distinct patches of a brilliant emerald-green appear upon the surface of the fluid, and, on emptying the basin, adhere to the sides, while the violet-tinted fluid from the aniline has little tendency to remain on the dish. Moreover, if the crude bases are heated with nitric acid until the aniline cannot but have been destroyed, on recovering the bases by distillation with an alkali, the fluid gives the green coloration with chloride of lime very distinctly. These reactions, and some other peculiarities of the volatile alkaloids of the pyridine series, as obtained from different sources, are as yet by no means well understood, but they are being actively studied, and can scarcely fail to yield results of sufficient value to repay examination.

On Bisulphite of Mercury. By Dr. W. WICKE.

Only the neutral sulphite of mercury has hitherto been known. Its composition, according to Gmelin, varies between HgO, SO^2 and $2\text{HgO}, \text{SO}^2$, according to the degree of saturation of the nitrate of mercury, which was mixed with the alkaline sulphite.

Bisulphite of mercury is easily obtained by pouring a saturated solution of bisulphite of soda over solid chloride of mercury. A brisk action immediately takes place, the result of which is the separation of the above-mentioned salt. This forms a white crystalline powder, composed of microscopic cubes attached together in bunches. It is tolerably soluble in water. On heating it, metallic mercury is of course separated. When heated dry, it begins to blacken below 212°F. , leaving metallic mercury. The cold aqueous solution is only precipitated by potash, by which a pale yellow basic salt is separated. Ammonia produces a finely-pulverulent white precipitate only when heated. Alkaline carbonates produce no change in the solution.

1.097 grm. of the salt, dried over sulphuric acid, was dissolved

in water, and the mercury thrown down by sulphuretted hydrogen. The sulphuret of mercury, when dried at 266°F. , weighed 0.7 gm. This contains 0.6034 mercury, or 55 per cent. The formula HgO , $2\text{SO}^2 + \text{HO}$ requires 55.24 per cent. of mercury. The salt consequently has the same composition as the corresponding potash-salt.

Other metallic chlorides were not decomposed in the same manner as chloride of mercury by the bisulphite of soda.—Liebig's *Annalen*, xcv. p. 176.

Investigation of some Derivatives of Naphthaline. By L. DUSART.

If a mixture be prepared of 2 parts of caustic potash and 1 part of lime, moistened with water so as to form a thick paste, and 1 part of protonitrated naphthaline be then added to the mixture by degrees, the mass immediately acquires a reddish-yellow colour, which is due to the formation of a peculiar acid. The mass is heated for about six hours, to a temperature which must not pass 212°F. , with the addition from time to time of a few drops of water to replace that which is driven off. At the end of this time the reaction is complete. The mass, washed by decantation until the water is no longer alkaline, is treated with an acid which separates the lime. The product thus obtained contains two matters, one yellow and crystallizable, the other brown and uncrystallizable. It is then distilled either by steam or by the open fire; the latter process is the most rapid, but furnishes a product of less purity, and in adopting it the operation must be stopped when red fumes begin to appear. The substance distilled forms crystals almost immediately.

This body, crystallized from boiling alcohol, furnishes long crystals of a straw-yellow colour; they are insipid, and of a weak aromatic odour. The substance fuses at $118^{\circ}\cdot 4\text{F.}$, boils at 554°F. , and passes over in great quantity at 572° to 608°F. , leaving a slight carbonaceous residuc. It is very soluble in alcohol, æther, and the hydrocarbons. Boiling water dissolves a small quantity of it, and allows it to crystallize on cooling. A very concentrated solution of potash acts upon it, furnishing a yellow acid. When distilled with a mixture of potash and lime, it furnishes a yellow odoriferous oil and long needles, which communicate a fine violet-blue colour to sulphuric acid. The oily matter dissolves readily in water; a few drops of perchloride of iron added to the solution give it an intense blue colour, and blue flakes are soon precipitated; these are changed to red by alkalies. Sulphuric acid dissolves it with a red colour. Sulphuret of ammonium gives a new alkaloid.

Phthalidine, $\text{C}^{16}\text{H}^9\text{N}$.—This is produced by the action of sulphuret of ammonium upon nitrated phthaline. The action is greatly assisted by keeping the solution at a temperature of about 122°F. on the water-bath for a few hours. After the alcohol has been driven off, the residuc is exhausted by dilute muriatic acid, and filtered after cooling. Potash gives rise at first to a white precipitate, which is redissolved in the excess of acid with a fine blue colour; a greater quantity of potash separates the alkaloid in the form of

flesh-coloured flakes, which soon change to red as they become aggregated. When washed and then crystallized by fusion, it is of the red colour of realgar; its odour resembles that of naphthalidine, and its taste is sharp and disagreeable.

It fuses at $71^{\circ}6$ F. At the moment of solidification the thermometer rises to $94^{\circ}1$ F., when it remains stationary. It begins to boil at about 491° F., but the temperature then rises rapidly, and the substance becomes partially altered, leaving a carbonaceous residue. It has no action upon reddened litmus, but its vapours immediately render the litmus blue. It dissolves in æther and alcohol, and also in considerable quantity in cold water, from which it is deposited in long needles. Its aqueous solution precipitates the salts of suboxide and protoxide of mercury.

It reduces nitrate of silver. A few drops of perchloride of iron give a fine blue colour; this reaction, which is very delicate, is common to morphine and salicylic acid. It furnishes well-crystallized salts with all the acids. Bichloride of platinum reduces it when the solution of the muriate is diluted, furnishing blue flakes, which become black in drying. If the solution of the muriate be very concentrated, this reagent furnishes fine yellow crystals, which undergo a change in drying. I have therefore been unable to determine the equivalent by the analysis of the platinum-salt.

Nitrophthalinic Acid, $C^{12}H^{14}NO^{10}$.—This is obtained in the preparation of the nitrated phthaline, by a secondary reaction of the potash upon that body. It is then contaminated by a foreign substance, which is difficult to get rid of. It may be more advantageously prepared by treating pure nitrophthaline with a very concentrated solution of potash. Its formation is exceedingly slow.

The potash-salt obtained is treated with water, filtered, and decomposed by muriatic acid. The acid is crystallized from a mixture of 1 part of water and 2 of alcohol, of spec. grav. 0.848; it furnishes on cooling small golden-yellow crystals, grouped in stars. The acid is inodorous; its taste at first is scarcely perceptible, but afterwards becomes sharp. When heated in a tube, it fuses, and leaves a carbonaceous residue.

The potash-salt is obtained by leaving the alcoholic solution to stand; it is deposited in small, reddish-yellow, mammillated crystals. It is very soluble in water, to which it gives a strong yellow colour. With nitrate of silver it furnishes a precipitate of a fine red colour; with acetate of lead, an orange-yellow precipitate, and a greenish-yellow precipitate with the salts of copper. Most of the metallic salts explode on the application of heat.—*Comptes Rendus*, Sept. 24, 1855, p. 493.

On the Composition of Eggs. By MM. VALENCIENNES and FRENÉY.

With regard to the eggs of birds, the authors first refer to the different properties exhibited by the albumen prepared from them. Thus, when coagulated, the albumen of the hen's egg is opaque and

pure white; but that of the plover's egg is transparent, opalescent, greenish, and much harder. They leave it undecided, however, whether in these cases different kinds of albumen are to be distinguished.

The vitelline, which is always combined with albumen in the yolk of birds' eggs, is prepared by them by treating the yolk of the hen's egg with cold water, in which the albumen dissolves, whilst the vitelline is precipitated; it is then washed with water, alcohol and æther. Thus prepared, its properties agreed with those previously ascribed to it; it dissolves with a violet colour in hot muriatic acid. The hardening of the yolk of birds' eggs when exposed to the air is attributed by the authors to the moisture of the atmosphere, which allows the vitelline to separate. They have made new analyses of vitelline, and indicate its agreement in composition with fibrine:—

	Vitelline.		Fibrine.
	I.	II.	
C	52.3	51.6	52.5
H	7.2	7.2	7.0
N	15.1	15.0	16.5
O	25.4	26.2	24.0

As a distinction between vitelline and fibrine, both which bodies agree in most of their properties, they state that the latter decomposes peroxide of hydrogen, which the former does not. Vitelline is a characteristic constituent of the eggs of birds, and does not occur in those of other animals.

Amongst the eggs of fishes, the authors first examined those of different cartilaginous fishes,—rays, torpedos and sharks. The white of these eggs scarcely contains any traces of albumen; the yolk consists of an albuminous fluid with some inorganic substances (especially chlorides and phosphates), a mechanically-mixed phosphorous oil, and a suspended substance which is insoluble in water, and to which they give the name of *ichthine*. In the eggs of the oviparous species, this forms small rectangular tables; in those of the viviparous species, oval grains or tables, which however are not crystalline. To prepare ichthine, they endeavoured to procure the yolk of the egg (of *Raia clavata*) as free as possible from contamination, and mixed this with a large quantity of water in which the ichthine grains were deposited; the latter were washed by decantation, and freed from fat by means of alcohol and æther. The ichthine grains are insoluble in water, alcohol and æther; they are transparent, even after lying for a long time in boiling water; they dissolve in all concentrated acids, but amongst the dilute acids only in acetic and phosphoric acids; they dissolve slowly in potash and soda, but apparently not in ammonia. The analysis of ichthine gave 50.2 to 51.0 of carbon, 6.7 to 7.8 of hydrogen, 14.7 to 15.4 of nitrogen, and 1.9 of phosphorus; it appears to contain no sulphur.

In the eggs of the osseous fishes the authors found other constituents, and the composition of their fluids undergoes changes whilst the egg is in the oviduct. The egg whilst still attached to the

ovary scarcely contains traces of albumen; when enclosed in the oviduct, it contains that substance in abundance. In the eggs of the carp the microscope showed, besides oil-drops, tabular deposits, similar to those previously described as ichthine; but in the osseous fishes these do not consist of ichthine, as they are soluble in water. The authors call this substance *ichthidine*, but they could not prepare it pure.

On the addition of a little water to the broken-up eggs of carp and many other fishes, taken whilst still in course of development, a fluid is first formed which only contains undissolved oil-drops; but on the addition of more water a body is separated, which may be united by shaking into a tenacious substance, insoluble in water. This substance, called *ichthuline* by the authors, was extracted with alcohol and æther, by which it was deprived of its tenacity and became pulverulent; in its chemical behaviour it is very similar to ichthine, and dissolves in muriatic acid without violet coloration. Its analysis gave 52.5 and 53.3 carbon, 8.0 and 8.3 hydrogen, 15.2 nitrogen, 0.6 phosphorus, and 1.0 sulphur. The completely developed eggs contained neither ichthidine nor ichthuline.

The authors also examined the eggs of reptiles. The eggs of the tortoises exhibit a great similarity of composition with those of the cartilaginous fishes; they contain but little white, with a very small amount of true albumen; the yelk contains much albumen, a phosphorous oil, and no ichthuline, but (although not in all the eggs) a granular body, insoluble in water, analogous to ichthine, which the authors denominate *emydine*. Emydine is distinguished from ichthine by its dissolving immediately in an aqueous solution of potash, and by its swelling up without dissolving in acetic acid; it dissolves in boiling muriatic acid without producing a violet colour. Its analysis gave 49.4 carbon, 7.4 hydrogen, 15.6 nitrogen, 27.6 oxygen and phosphorus, with an amount of 1 per cent. of lime-salts. The authors regard emydine as isomeric with ichthine.

The yelk of the eggs of lizards appears to have some similarity with that of the bird's egg. With regard to the eggs of snakes and vipers, frogs and salamanders, crabs and lobsters, spiders and ants, and of the mollusca, the results obtained were not sufficiently definite to allow of their being given in an abstract. But in reference to the eggs of the crabs and lobsters, we may mention that, according to Valenciennes and Fremy, these eggs contain the substance which causes the shells of those animals to become red when boiled. In the eggs it is dissolved in the albumen; and when the crushed eggs are diluted with water, the colouring matter is thrown down in the form of a green resinous substance, which reddens in drying, even *in vacuo*, and by the action of salts, which attract water. The same effect is produced by alcohol and æther, and lastly by rubbing with a solid body. In the red state the colouring matter may easily be obtained by heating the albuminous fluid in which it is dissolved, and extracting it by means of alcohol from the coagulated albumen which surrounds it.—*Comptes Rendus*, 1854, xxxviii. pp. 469, 525, 570; Liebig's *Jahresbericht*, 1854, p. 684.

On Arabine. By M. NEUBAUER.

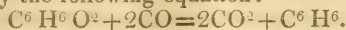
During an investigation of the ashes of various kinds of gums Löwenthal prepared arabine by the process employed by Schmid, for the purification of tragacanth, &c. This consisted in dissolving gum-arabic in cold water, so as to form as thick a mucilage as possible, filtering this, and adding muriatic acid until a strong acid reaction was produced, when the arabine was precipitated by means of alcohol, and these solutions and precipitations were repeated several times. The arabine, thus prepared in the form of a white amorphous mass, readily dissolves in water whilst still moist, forming a mucilage; the aqueous solution is not precipitated by alcohol, unless after the addition of muriatic acid or solution of chloride of sodium, when precipitation takes place immediately. The aqueous solution of pure arabine exhibits an acid reaction. When dried in the air, arabine becomes glassy and transparent, and gradually loses its solubility in water; when dried at 212° F., it is no longer soluble in water, but only swells up in a gelatinous form in that fluid.

The composition of arabine, dried at 212° F., agreed with the formula $C^{12}H^{11}O^{11}$; at a higher temperature it appears to give off no more water until it begins to decompose. Arabine, dried at 212° F., with an acid reaction, when mixed with lime-water until an alkaline reaction was produced, soon regained its acid reaction. From the fluid obtained by the action of lime-water upon arabine, alcohol separated a lime compound, which readily dissolved in water to form a mucilage, and when dried at 212° F. had the formula $CaO, 6C^{12}H^{10}O^{10}$. From the fluid obtained by boiling arabine with water and an excess of hydrated lime, alcohol separated another lime compound, which also dissolved readily in water; this, when dried at 212° F., consisted of $CaO, 2C^{12}H^{10}O^{10}$. By treating arabine with baryta-water (not in excess), and precipitating the fluid with alcohol, a baryta compound was obtained, which when dried at 212° F. contained 11.0 to 11.2 per cent. of baryta. An excess of baryta-water furnished a compound with 17.5 to 17.8 per cent. of baryta, the composition of which, when dried at 212° F., approached very closely to the formula $BaO, 2C^{12}H^{10}O^{10}$. A potash compound, precipitated by alcohol from a solution of arabine in potash, had the constitution $KO, 3C^{12}H^{10}O^{10}$ when dried at 212° F. Basic acetate of lead precipitates a lead compound from the aqueous solution of arabine; this becomes of a slight yellowish colour when dried at 212° F., and of a strong brown at 320° to 356° F. Portions prepared at different times, and dried at 212° F., contained 27.0, 30.5 to 30.8, and 30.5 to 30.7 per cent. of oxide of lead; the composition of the latter preparations approaches the formula $2PbO, 3C^{12}H^{10}O^{10}$.—*Journ. für Prakt. Chem.*, lxii. p. 193.

Note on a new Mode of producing Propylene. By L. DUSART.

If a mixture of an alkaline acetate and oxalate be distilled in such a manner as to place the acetone formed in contact, when in the nascent state, with the oxide of carbon produced by the decomposi-

tion of the oxalate, deoxidation of the acetone takes place, with formation of a carbonate, and a gas passes which is absorbable by bromine, and which is nothing but propylene. The reaction may be represented by the following equation:—



Nevertheless we by no means obtain the quantity of propylene indicated by theory. The decomposition of the two salts is not simultaneous, and the oily matter observed in the preparation of acetone is always produced.

The process adopted is as follows:—Equivalent portions of acetate of lime and oxalate of potash are taken; the oxalate is dissolved in water, and the acetate of lime added to it, so as to produce oxalate of lime and acetate of potash. The liquid is evaporated, and kept in continual motion to obtain an intimate mixture. When dried as much as possible, the mass is put into a retort, which is heated over a moderate fire, and the quantity of propylene appears to be increased if the temperature be gradually and slowly raised. The gas passes first into a flask filled with carded cotton, then into a flask containing sulphuric acid to absorb the oily matter, and it is afterwards condensed in bromine after being washed in water. A kilogramme of acetate of lime furnishes about 60 grms. of crude propylene.

The liquid obtained is washed with potash, and distilled directly; it is then agitated again with an alkaline solution, which saturates the hydrobromic acid formed during the distillation. It is dried over chloride of calcium, and distilled with a thermometer inserted.

Bromide of propylene forms about two-thirds of the product. It possesses the odour and the boiling-point (293°F.) of the propylene obtained from amylic alcohol.

The compound $\text{C}^6\text{H}^6\text{Br}$, obtained by the action of an alcoholic solution of potash upon the preceding product, when heated in a tube with sulphocyanide of potassium, furnished the essential oil of mustard, which has recently been produced by M. Berthelot with iodized propylene obtained from glycerine. It is therefore possible by a simple deoxidation of acetone, to ascend from the acetic to the propylic series, and to reproduce alcohol, if instead of collecting the hydrocarbon in bromine, we cause it to be absorbed by sulphuric acid, and distil it with water, according to the ingenious process of this chemist.—*Comptes Rendus*, Sept. 24, 1855, p. 495.

ANALYTICAL CHEMISTRY.

On Molybdate of Lead, and its employment as a Reagent for Phosphoric Acid. By Dr. W. WICKE.

THE following method for the decomposition of the native molybdate of lead has proved to be advantageous, and scarcely any other with which I am acquainted can furnish so great a quantity of molybdic acid. The finely-powdered mineral is treated with about three times its quantity of concentrated ammonia, and sulphuretted hydrogen is passed into the fluid until a dark brownish-

red colour is produced. We have then a compound of sulphuret of ammonium and sulphuret of molybdenum. A black crystalline powder lies at the bottom, together with a green salt, which when taken out of the fluid forms dark green, nearly transparent prisms. It is doubtless the sulpho-salt, analogous in its composition to K_2S , $\text{MoS}_3 + 4\text{HO}$. I would have determined its composition if it had not been so very alterable. The crystals cannot be dried so rapidly as to prevent their losing their colour, and forming brown spots upon the paper. They dissolve readily in water, with an intense reddish-brown colour.

If the above-mentioned black metallic powder be washed with water, and treated again with ammonia and sulphuretted hydrogen, a complete decomposition of the native molybdate is effected. If the solution, diluted with at least twice its quantity of water, be mixed with muriatic acid, the sulphuret of molybdenum is thrown down in the form of a brown flocculent precipitate, from which pure molybdic acid may be obtained in the ordinary way*.

Molybdate of lead may be employed as a reagent for phosphoric acid instead of molybdate of ammonia, and with equally good results. It is first of all tested as to its freedom from phosphates; muriatic acid, and afterwards a few drops of ammonia are added, and it is then heated. The samples which I have tested for this impurity proved to be free from it, and molybdate of lead might consequently be employed immediately as a reagent. Only a very small quantity of molybdate of lead, and consequently only a little ammonia, is required; but an excess of muriatic acid must be used. The fluid to be tested for phosphoric acid, when boiled with this mixture, furnishes in a few moments, if phosphoric acid be present, the characteristic yellow precipitate of phosphate and molybdate of ammonia. This is also produced with sulphuric acid, but not, or very slowly, with nitric acid. Muriatic acid is the best, particularly as the chloride of lead formed remains dissolved, and the yellow salt is deposited from a clear fluid.

When a fluid containing sulphuretted hydrogen is to be tested for phosphoric acid, the former must be previously destroyed by boiling with nitromuriatic acid. Otherwise a portion of the molybdic acid would be reduced, and a blue fluid (molybdate of oxide of molybdenum) would be obtained.—Liebig's *Annalen*, xcv. p. 373.

On a Reaction of Protosalts of Iron in presence of Copper.

By J. W. SLATER, Esq.†

Protosalts of iron give, as is well known, a pale blue precipitate with the ferrocyanide of potassium under ordinary circumstances. If however a soluble salt of copper be present in considerable amount, a dense, deep blue precipitate is at once determined,

* The decomposition of molybdate of lead may also be readily effected by heating the finely-powdered ore with strong solution of soda, and gradually adding flowers of sulphur. In this manner all the molybdenum is obtained in solution as sulphuret.

† Communicated by the Author.

scarcely to be distinguished in appearance from that furnished by a ferric salt. The characteristic reaction of copper is thus lost, even when its amount reaches 50 per cent. Beyond that proportion the red-brown ferrocyanide of copper falls first, if the ferrocyanide of potassium be cautiously added. The deep blue precipitate yielded by the mixed salts undergoes no change of colour on long standing. A persalt of iron along with copper gives with the ferrocyanide of potassium a dirty olive precipitate, intermediate in colour between those yielded by the two salts when alone.

Sheffield Mechanics' Institution,
October 1855.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Glasgow, September 12th, 1855.

On some points connected with Agricultural Chemistry.
By J. B. LAWES, F.R.S., and Dr. J. H. GILBERT, F.C.S.

THE authors explained that their subject was necessarily somewhat controversial, for Baron Liebig had recently published a criticism on their experiments and opinions which had been circulated very freely in England, France, Germany, and America; and, from the well-merited reputation of that distinguished chemist, his statements and opinions had been echoed almost unexamined by numerous writers, both in the technical and general press. To those statements and opinions, therefore, the authors now proposed to address themselves. They would first call attention, however, to the unfairness of an article on the question at issue in a recent Number of the Journal of the Highland Society of Scotland*; as by doing so they would be naturally led to a proper definition of the subject before them. They explained that it was *agriculture*, not normal vegetation; that is, the growth of plants *under cultivation*, and not their growth in circumstances under which every element necessary for their development had to be specially provided. In other words, they presupposed as the preliminary conditions of their inquiry, a soil under ordinary cultivation, and an atmosphere—each yielding its quota to the result. Indeed, Baron Liebig had himself defined the province of agricultural chemistry to be, that of producing *more* corn and *more* meat, and not simply corn and meat, which had been produced for centuries without her aid.

Looking at the subject in this point of view, the authors maintained, as a fundamental fact, that the composition of agricultural vegetable produce was no direct guide in the choice of manure for

* Professor Anderson, on the part of the Highland Society, repudiated its responsibility for the article in question; and Mr. Robert Russell of Kilwhiss also disclaimed all connexion with its authorship.

the various crops grown in rotation,—that which was required being, simply to meet the resultant deficit for the artificial production of that *margin of produce* which distinguished agriculture, as practised in this country, from natural vegetation,—or from produce obtained for the purposes of export, without any return to the land by home manures.

Those of their experiments which had been passed under criticism by Baron Liebig, were taken with others by their side, to illustrate the conclusions to which the authors had arrived. They first brought a summary of the results of their experiments on the growth of wheat by different chemical manures, during many consecutive years; and they maintained, that inasmuch as by means of such manures they could raise the produce by from ten to twenty bushels per acre over the unmanured produce, and indeed far exceed the result obtained by the annual supply of farm-yard manure,—that this being the case, the objection of Baron Liebig, that their soil was naturally so rich as to be unfit for experiment, must be considered to be entirely without foundation. They then illustrated by tables and diagrams of results, by reference to which Baron Liebig had endeavoured to prove the contrary,—1, “that the mineral constituents of wheat cannot, by themselves, increase the fertility of land;” and 2, “that the produce in grain and straw is rather proportional to the supply of ammonia.” So far as it went, they fully accepted the above definition of their conclusions as given by Baron Liebig, subject of course to the qualifications which their own papers would indicate. But they utterly repudiated that definition, when understood in the manner assumed by Baron Liebig when summing up and giving his verdict on their opinions at the conclusion of his treatise. They next showed, by reference to tables, that nitrogenous manures, whether applied in the form of ammoniacal salts, nitrate of soda, or rape-cake, had a great effect in the increase of produce of *barley* also, the next in importance of the cereal grains.

Turning to *turnips*, the type of the root-crops grown in alternation with the Cereals, they submitted, that Baron Liebig's statement, that phosphates were the only manures which they had found to increase the growth of the turnip, was directly contrary to the whole tenor of their papers on the subject; in which they had maintained the absolute necessity of providing matters yielding both assimilable carbon and nitrogen within the soil, for the production of a full amount of the crop in question. They did maintain, however, that phosphoric or phosphatic manures had an action on the development of the underground fibrous feeders of the plant, and consequently on its rapid growth and development, which could not be accounted for by the mere supposition of supplying the actual constituents of the crop to be grown and removed from the land. They illustrated, that in their experiments they had the very circumstances provided, which had been demanded by Baron Liebig as necessary for the support of their conclusions; and thus it was proved, that even where there existed in the land a residue of phosphates from previous manuring more than would be contained in many heavy crops, still an annual

additional supply gave annually a considerable increase of produce. They further pointed out, that Baron Liebig had endeavoured to substantiate his objections by comparisons which they showed to be quite inadmissible,—whilst one main argument he had founded upon a mere misprint, which reference to the succeeding tables would at once have explained. His argument on the point in question was therefore simply reversed. They next illustrated by a collective table, the action of manures on some of the most important crops of rotation; including wheat and barley as Cereals, turnips as a root-crop, and beans and clover as leguminous crops. From this table it appeared, that whilst mineral manures alone had little or no effect in increasing the produce of wheat and barley, grown respectively in succession, nitrogenous manures, on the other hand, yielded most striking results. And here attention was called to the fact, that these manures had a similar effect in raising the produce of corn after the exhaustion of corn cropping, on the farm of the Earl of Leicester at Holkham, of which the surface soil was thin and light, but with a subsoil of excellent marl; and also at the farm of the Duke of Bedford at Woburn, on a soil and subsoil naturally of the poorest possible description. And they further maintained, that these results of direct experiment on different soils, were perfectly in accordance with the general experience of practical farming all over the country, as to what was the predominant characteristic of *corn exhaustion*. In the experiments quoted, mineral manures were, however, of course found to give a further increment of increase, when the nitrogenous manure employed was in excessive quantity.

With *turnips*, again, superphosphate of lime had given an average increase during a series of years of more than seven tons of the bulb; and the addition of alkalies to this, had even diminished the amount of increase. Ammonia-salts alone, on the other hand, had only given a few hundred weights of increase, instead of more than as many tons by the phosphatic manure. The mixture of both mineral and ammoniacal manures had, however, given a better produce still; though not equal to that which was obtained when there was also a liberal supply of carbonaceous organic matter within the soil. Turning to *beans* and *clover*, nitrogenous manures which had been so beneficial to the Cereals, and phosphates which had been so much so to the turnips, had here comparatively little effect. The constituent of manure which acted in the most characteristic manner with these leguminous crops was the alkali *potass*; which, when used as a direct manure to soil of a similar description, had comparatively little effect on the increase of the growth of the Cereals or turnips.

In these remarkable facts, though the experiments cited were by no means to be taken as examples of manuring, the authors considered there was afforded an interesting clue to the principles involved in *manuring, fallow, and the rotation of crops*.

They next called attention to the analysis of three actual rotations; the course in each case being, turnips, barley, clover, wheat. In one instance, the rotation commenced without manure; in the second with superphosphate of lime alone; and in the third with a mixed

and pretty full manuring. It appeared, that in each case the *clover* grown between the barley and the wheat (the intervention of which instead of the immediate succession of the wheat would greatly increase the produce of the latter) removed from the land very much more of phosphoric acid, of potass, of lime, and of magnesia—in fact of every important mineral constituent except silica—than either the preceding barley or the succeeding wheat. Hence it was maintained, that the effect of this leguminous crop in rotation as a preparation for wheat, could not be, according to the theory of Baron Liebig, to increase the available supply of, or to conserve within the soil, the important mineral constituents of the crop. Unless indeed in the case of *silica*; which, however, Baron Liebig had himself maintained would never be wanting in sufficient quantity in any soil, provided there were a sufficiency of available alkalies present. Taking these facts, together with those indicating the most important manuring for the Cereals, as well as with others relating to the composition and known circumstances of growth of the leguminous crops, it could only be concluded, that the *clover* had accumulated from the atmosphere *within the soil*, a supply of available nitrogen to a great extent exhausted by the growth of the previous Cereal, *barley*, and so essential for the succeeding Cereal, *wheat*.

Finally, attention was called to the fact, that but a comparatively small proportion of the nitrogen supplied in manure for the growth of Cereals, was recovered in the increase produced. They showed by a table that the loss of nitrogen was greater or less according to the amount of it supplied in manure, and to the conditions favourable or otherwise as to mineral supply, character of the season, &c. Under the most favourable conditions for the full effect of the supplied nitrogen, that is, with a full supply of minerals and a limited supply of nitrogen, they had only recovered in the increase about half the nitrogen contained in the manure. But when nitrogen was supplied in quantity sufficient to yield a full crop for any given season, they had obtained little more than one-third of the supplied nitrogen in the increase. And, inasmuch as, when the amount of nitrogen employed was not very great, the one-half or two-thirds which was not recovered in the increase obtained in the year of the application of the manure, had little or no effect on the next crop, it could not be supposed that the bulk of this excess of nitrogen still remained within the soil. It was worthy of remark, that vegetable physiologists had frequently recorded an evolution of nitrogen from the leaves of plants during their growth, beyond that which was due to the atmosphere with which they had been supplied. But as it had not yet been satisfactorily demonstrated, that the Cereals gave off more nitrogen in this way than the leguminous crops of rotation, further experiment was needed before the loss in question, and consequently the varying characters in this respect of the different plants in rotation, could with full confidence be explained by reference to the functional action in question. The only explanation which had been suggested *as special to the Cereals*, was that proposed by Mr. Way, namely, that the silica required by

these plants is taken up as a silicate of which ammonia is a base, and that this alkali or its constituents is evolved upon the fixation of the silica within the plant. It was, however, perhaps, not very favourable to this view, that the authors had found that water containing salts of ammonia dissolved less silica than pure water, when percolated through a given bulk of soil. It must be admitted, however, that although the explanation of this loss of nitrogen with the cereals might require further investigation, which the authors had hoped to devote to it, yet, as in the case of other crops, they had recovered in a series of years a much larger proportion of the supplied nitrogen, they considered that the loss in question could not be wholly due either to drainage of soluble or the evaporation of volatile compounds of nitrogen; but that the fact of a considerable loss in the production of a full crop of the cereal grains must be looked upon as an important and fundamental item in studying the rationale of agricultural practices.

Upon the whole, they concluded:—

1. That the manure indicated by the resultant requirements of British agriculture, has no *direct connexion* with the composition of the mineral substances collectively found in the ashes of the produce grown on, or exported from the farm; and that the direct mineral manures which are required, are not advantageously applied for the direct reproduction of the exported corn, but should be used for the green or *fallow crops*, an office of which it is, to collect from the atmosphere, or to conserve on the farm, *nitrogen* for the increased growth of the saleable cereal grains.

2. That the nitrogen required to be provided *within the soil* for this purpose, is far greater than that contained in the increase of produce obtained by it.

3. That the effects of *fallow* in increasing the growth of the saleable cereal grains (so far as they are chemical), are not measurable by the amount of the additional mineral food of plants liberated thereby, these being under ordinary cultivation in excess of the assimilable nitrogen existing in, or condensed within the soil in the same period of time; the amount of which latter therefore—the *available nitrogen*—is the measure of the increased produce of corn which will be obtained.

4. That the beneficial effects of *rotation*, in increasing the production of saleable produce (so far as they are chemical), are *not* explained by the fact of one plant taking from the soil more of the different mineral constituents than another, but depend on the property of the so-called green or *fallow* crops bringing on, or conserving upon the farm, more of substance rich in nitrogen than is yielded to them in manure, whilst the crops to which they are subservient are both largely exported from the farm, and yield in their increase considerably less of nitrogen than is given to them in manure.

5. In a word,—That in the existing condition of British agriculture, a full production of the *saleable cereal grains*, with at the same time other exportable produce, is only attained—whether by *manures*, *fallow*, or *rotation*—by an accumulation of available nitrogen (nor-

mally an *atmospheric* constituent), *within the soil itself*.—*Communicated by the Authors.*

Abstract of the Report on the Influence of the Solar Radiations on the Vital Powers of Plants growing under different Atmospheric Conditions.—Part III. *By* J. H. GLADSTONE, Ph.D., F.R.S.

In the present report the author addressed himself to the solution of certain questions that had been suggested during the progress of his previous inquiries. Thus when peas and wheat had been grown under colourless, blue, red, yellow, obscured colourless, and obscured yellow glasses, and in total darkness, several definite results had been arrived at, among which was the following:—"the cutting off of the chemical ray facilitates in a marked manner the process of germination, and that both in reference to the protrusion of the radicle, and the evolution of the plume." The experiments, however, were open to the objection, that the seeds, in order to be fairly exposed to the various lights, were not surrounded by any soil. Another series was therefore started with a proper supply of garden-mould. The results obtained were not so definite as on the former occasion, and tended rather to oppose the conclusion quoted above. Accordingly an experiment was instituted for the purpose of determining whether the chemical ray exerted a different influence according to whether soil was present or absent. Two sets of colourless, blue, and yellow glasses were taken; under the one wheat and peas were grown without soil, under the other with soil. Particular observations were made and recorded; from which it appeared that the three different lights exerted the same respective influence on the germinating seeds, whether they were enveloped in mould or otherwise. In respect to the wheat, it was found that the smallest number of seeds had germinated under the influence of the chemical ray, yet that that ray was favourable to a healthy growth up to a certain point, after which the plant seemed to require the luminous or calorific rays in order to profit by the soil. In respect to the peas, it was found that those growing under the blue glass always displayed an inferiority; the most healthy plants were produced when the seeds were exposed to all the influences of the solar beam, and the deprivation of the luminous principle proved fatal to them in their more mature growth, although the removal of the chemical ray had little effect.

In a former report the question was proposed, "Does carbonic acid act specifically in the prevention of germination, or merely by the exclusion of oxygen?" This was now answered by substituting that gas for the nitrogen in the air, and observing whether seeds germinated equally well in such an atmosphere. It was found that they did not germinate, but became rotten.

The report concluded by stating, that, on account of the great difficulties of the inquiry, the conclusions arrived at during the investigation must not be generalized without the greatest caution.—*Communicated by the Author.*

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of Fulminating Mercury and Isocyanuric Acid.
By L. SCHISCHKOFF.

THE author has analysed fulminating mercury, and by treating it with alkaline iodides and chlorides, has obtained the same acid and salts recently described by Liebig*. M. Schischkoff's paper was published two months before Liebig's notice.

According to his analyses, the composition of fulminating mercury corresponds exactly with that of fulminating silver, when it has been prepared by the treatment of a solution of mercury in an excess of nitric acid. If it be allowed to crystallize from water, it is obtained in white or slightly yellowish silky needles, which contain 1 atom of water of crystallization when dried at 212° F. The drying, even at this temperature, is attended with the greatest danger. The analysis of fulminating mercury, as obtained in the preparation from alcohol without recrystallization from water, gave,—

						The salt crystallized from water.
C	8.48		4 = 24		8.45	
N	9.92		2	28	9.86	
Hg	70.08	70.58	2	200	70.42	68.25
O	..		4	32	11.27	

From this the formula is $C^4 N^2 Hg^2 O^4$; and that of the salt crystallized from water is $C^4 N^2 Hg^2 O^4 + HO$.

The author has evidently been influenced by the same ideas which led Liebig to the discovery of the same body. His design was to get the mercury out of the compound by mutual decomposition, in order to see what the residue would consist of. For this purpose he treated the fulminating mercury with iodide of potassium. When a weak solution of this salt is heated with fulminating mercury, the latter dissolves; if the heat be only a gentle one, the solution acquires a yellow colour, but when more strongly heated, the fluid becomes darker, and lastly cherry-red. In both cases, small, white, shining laminae separate on cooling; these are extremely explosive. This salt is insoluble in water and alcohol; when exposed to daylight in the dry state, it gradually becomes red in consequence of the formation of small crystals of iodide of mercury.

1.578 grm. of this compound, calcined with caustic lime, gave

* Chem. Gaz., 1855, p. 341.

0.827 grm. of metallic mercury, or 52.4 per cent. The formula $2C^4 N^2 Hg^2 O^4 + KI$ represents 54.4 per cent. Chloride of potassium, sodium and ammonium give similar compounds under the same circumstances.

When a solution of fulminating mercury in iodide of potassium is heated to boiling, it gradually acquires a darker colour, and lastly, an abundant brown precipitate is formed in the fluid; this is evidently contaminated with red iodide of mercury. If the fluid be then filtered and evaporated on the water-bath, ammonia is evolved on the attainment of a certain degree of concentration. On the cooling of the fluid, well-formed crystals of periodide of mercury are deposited, and simultaneously with these, crystals of the potash-salt of a new organic acid.

As the brown precipitate thus obtained is evidently contaminated with periodide of mercury, the solubility of chloride of mercury induced the author to try whether chloride of potassium might be substituted for iodide of potassium, hoping in this manner to obtain a more distinct reaction; and it appeared that the formation of the new acid takes place equally well when chloride of potassium or sodium is employed.

The reaction takes place in the following manner:—A nearly saturated solution of chloride of potassium is heated to boiling. Fulminating mercury is then added in small portions, with constant stirring; in this way the author added 2 parts of moist fulminating mercury to 1 part of chloride of potassium. It is not necessary that the fluid should boil strongly; when the whole is of a light yellow colour, and no more fulminating mercury remains at the bottom of the dish, the reaction may be considered as complete.

The yellow colour of the fluid arises from a precipitate formed in it; this readily settles, and must be separated by a hot filter, as the fluid very readily solidifies in cooling, in consequence of the separation of the principal product, a caseous body, which is very difficult of solution in cold water. The precipitate on the filter is washed with hot water; on the concentration of the washing water, as well as of the mother-liquor poured from the caseous body which is formed on cooling, a further quantity of the latter is obtained. In the second and third coolings, the caseous body, mixed with a small quantity of the yellow precipitate, is obtained, and may afterwards be purified by solution in boiling water. At the end a mother-liquor remains, containing an excess of chloride of potassium with a considerable quantity of perchloride of mercury.

The principal product of this reaction, the caseous body, contains the potash-salt above-mentioned in combination with peroxide of mercury. When water is poured over it, and sulphuretted hydrogen is passed through the mixture, sulphuret of mercury is separated, simultaneously with crystals of the potash-salt; to obtain the latter, the whole fluid must be heated, filtered through a hot filter, and left to crystallize. On cooling, shining colourless crystals are deposited, and a further quantity of these is obtained by repeated evaporation and cooling of the mother-liquor. In this way the author obtained

more than 20 grms. of the potash-salt from 150 grms. of fulminating mercury.

The caseous body may be obtained directly by heating a solution of the potash-salt with oxide of mercury (especially the yellow oxide), and filtering the hot solution. It is worthy of notice that the mercury exists in a peculiar condition in this caseous body, as it is not separated even by boiling with copper, and neither caustic potash nor iodide of potassium exert their usual influence upon salts of mercury in this case.

When iodide of potassium is employed instead of chloride of potassium in preparing the potash-salt of the new acid, the caseous body is not produced: the action of chloride of potassium is also distinguished by the circumstances, that no evolution of ammonia is perceptible during the evaporation of the fluid poured from the precipitate, and that no effervescence takes place on the addition of an acid. But as the quantity of acid obtained is the same in both cases, the evolution of carbonic acid and ammonia, when iodide of potassium is employed, must be ascribed to a decomposition of the brown precipitate, which consequently must contain carbon and nitrogen. The precipitate which is obtained by the action of iodide of potassium does actually contain these elements; and in all probability the yellow precipitate only differs from the brown one in containing chlorine instead of iodine.

The organic potash-salt obtained by this reaction has the following properties:—It dissolves in 10 parts of cold, and a much smaller proportion of boiling water. When a hot saturated solution is rapidly cooled, it sets in consequence of the formation of very small silky needles; but by gentle evaporation the salt is obtained in large and very regular crystals. The salt is insoluble in alcohol and æther. When heated to 437° F., it undergoes no change, but with a stronger heat much hydrocyanic acid is evolved, the mass first melting; it afterwards becomes black, and finally explodes with a red flame. When slowly decomposed in a covered crucible by a heat gradually raised to redness, the salt furnishes a pure white cyanate of potash with a mixture of cyanide of potassium. A solution of the potash-salt, mixed with nitrate of silver, produces a silver-salt in the form of a thick crystalline precipitate, which is soluble in boiling water, and on cooling crystallizes in beautiful, white, silky needles, grouped in bundles.

This salt is not blackened by light, nor does it undergo any change when heated to 302° F.; at a higher temperature it explodes without noise with evolution of hydrocyanic acid. The analyses of this salt gave,—

	I.	II.	III.		
C	15·35	14·88	15·05	6 =	15·25
N	17·93	..	..	3	17·79
H	0·98	0·98	0·89	2	0·84
O	..	..	..	6	20·36
Ag	45·54	45·32	..	1	45·76

z 2

The acid separated from this salt by means of sulphuretted hydrogen or muriatic acid is denominated by the author *isocyanuric acid*; it is evidently the fulminuric acid of Liebig. It is soluble in water, alcohol and æther; the aqueous solution has an acid reaction, and possesses an agreeable taste; when evaporated it becomes of the density of a syrup, and afterwards sets into an indistinctly crystalline mass. The acid undergoes no change in the air; it separates in a few days from a saturated alcoholic solution in the form of small colourless prisms.

The acid contains no water of crystallization; when heated to 302° F., it is decomposed in the same way as its salts. It decomposes the carbonates with effervescence; its concentrated solution has the property of giving an intense rose-red colour to pine-wood. Its analysis gave,—

C	28.16	6 =	27.90
N	32.66	3	32.55
H	2.44	3	2.52
O	..	6	37.21

The soda-salt of this acid is considerably more easy of solution in water than the potash-salt; it is also soluble in alcohol. When its aqueous solution is slowly evaporated, it crystallizes in long prisms.

The ammonia-salt is isomorphous with, and very similar to, the potash-salt, but is somewhat more soluble in cold water; on the cooling of its hot solution, it crystallizes in fine, extremely shining needles. When heated to 302° F., it undergoes no change; but when heated beyond this point, it explodes like the other salts of isocyanuric acid :—

C	24.57	6 =	24.65
H	4.05	6	4.10
N	37.80	4	38.35
O	..	6	32.88

The potash-salt, like the salts of silver and ammonia, contains 1 equiv. of metal.

A concentrated solution of the isocyanurate of ammonia, mixed with a concentrated solution of chloride of barium, produces the baryta-salt of this acid in small prisms on cooling.

Isocyanuric acid and its salts are not precipitated by neutral acetate of lead; nor is this effect produced by solution of cadmium. Basic acetate of lead, on the contrary, immediately produces a precipitate. Proto- and per-salts of mercury do not precipitate this acid; peroxide of mercury, when heated with a solution of the acid, dissolves in it, and on cooling a mass separates, which resembles the caseous body above mentioned.

The most characteristic salt of isocyanuric acid is the salt of copper and ammonia. To prepare this, a solution of isocyanuric acid is mixed with a solution of a salt of copper in an excess of ammonia, and the whole heated to boiling. On cooling, beautiful,

shining, dark blue prisms are deposited; these undergo no change in the air, or even when heated to 302° F., but at a higher temperature they are decomposed with an explosion. This salt is nearly insoluble in water, and very difficult of solution in ammonia, so that extremely small quantities of isocyanuric acid can be separated in this form. Cyanuric acid, as is well known, furnishes a similar salt, but of different colour, under the same circumstances.

Isocyanuric acid combines with urea and aniline; in both cases crystalline bodies are produced. The aniline salt, which is soluble in water and alcohol, is obtained when alcoholic solutions of the acid and aniline are mixed together; very fine entangled crystals are produced. Some experiments of the author's also seem to leave no doubt that there exists an æther of this acid.

Isocyanuric acid and its salts explode when heated. Strong sulphuric acid decomposes them without blackening; by this agent ammonia is produced in the fluid, and a gas, consisting of carbonic acid and carbonic oxide, is evolved. Weak muriatic acid has scarcely any action upon the salts of isocyanuric acid; but strong muriatic acid decomposes them, with formation of ammonia and evolution of carbonic acid. After the saturation of the excess of muriatic acid, a white precipitate is formed in the fluid by salts of lime or baryta; but if the action of the muriatic acid has been long continued, and the fluid has been afterwards evaporated to dryness, this precipitate is not produced.

Caustic baryta decomposes isocyanuric acid and its salts when heated; ammonia is evolved, and a white precipitate is formed. This precipitate contains carbonate of baryta, as it dissolves in acids (muriatic and nitric), with evolution of carbonic acid. After the neutralization of the excess of acid employed by ammonia, a precipitate is deposited, which is probably the same produced by a solution of a baryta-salt in isocyanuric acid, decomposed by means of muriatic acid.

When caustic potash is heated with isocyanuric acid or its salts, much ammonia is evolved; carbonate of potash remains in solution, and after neutralization by an acid, neither chloride of calcium nor nitrate of silver produces a precipitate. The precipitate above mentioned as being produced by salts of lime and baryta contains nitrogen, for when heated with caustic potash it evolves ammonia. Nitrous acid, passed through a solution of isocyanuric acid, decomposes it with violent evolution of gas (CO^2 and $\text{N}^?$); when this action is concluded, an acid remains in solution, which on the addition of nitrate of silver furnishes an insoluble salt containing nitrogen. Lime-salts do not precipitate this acid. Hydrosulphuret of ammonium ($\text{H}^2 \text{S}^2 \text{NH}^3$) and hydrosulphuret of potassium (KHS^2) have no action upon isocyanuric acid, even when boiled. When protacetate of iron is heated with the salts of isocyanuric acid, beautiful pale green crystals of isocyanurate of iron are separated.

[To be continued.]

Examination of Veratrine and some of its Salts. By G. MERCK.

Veratrine has been analysed by Couërbe, and by Pelletier and Dumas. The former obtained on an average 69·6 per cent. of carbon and 7·2 per cent. of hydrogen (re-calculated for $C=6$); he proposes the formula $C^{34} H^{43} N^2 O^6$ ($H=0\cdot623$). The latter obtained 65·76 per cent. of carbon and 8·54 per cent. of hydrogen (re-calculated for $C=6$). The diversity of these numbers, and the circumstance of my succeeding in preparing veratrine in considerable quantity beautifully crystallized, and therefore perfectly pure, whilst the above-mentioned chemists operated upon a resinous body, induced me to submit this substance to a fresh examination.

The veratrine employed was prepared in the following manner:—A dilute solution of pure commercial veratrine in alcohol containing as much water as possible was evaporated on the water-bath at a gentle heat, during which a portion separated in the form of a white crystalline powder mixed with a brown resinous mass. The latter could be got rid of by washing with cold alcohol. By dissolving the crystalline veratrine thus obtained in highly-rectified alcohol, and leaving the solution to evaporate spontaneously, I obtained it in crystals of about half an inch long, in the form of rhombic prisms*.

The crystals, which are at first perfectly colourless and transparent, soon effloresce in the air, becoming porcellanous and very pulverizable. They are insoluble in boiling water, but are thereby rendered opaque, and lose their form without fusing. They are readily soluble in alcohol and æther, especially the latter. When concentrated sulphuric acid is poured over them, they colour it first yellow, and then carmine-red. With concentrated muriatic acid they give a dark violet solution, especially when heated; on the surface of this small oily drops are formed.

Veratrine neutralizes the dilute acids completely, furnishing colourless solutions, which dry into gum-like masses. Couërbe obtained the sulphate and muriate in a crystalline form, but I did not succeed in doing so. The solution in muriatic acid gives with chloride of platinum a precipitate which is soluble in a large quantity of water; with chloride of gold it gives an insoluble, and with perchloride of mercury a crystalline precipitate.

The analysis of veratrine, dried at $212^{\circ} F.$, gave,—

	I.	II.	III.	IV	V.		
C	64·73	64·51	64·99	65·00	..	64=384	64·86
H	8·84	8·55	8·76	8·70	..	52 52	8·78
N	..	..	..	..	5·5	2 28	4·73
O	..	..	..	..	..	16 128	21·63

These numbers lead to the formula $C^{64} H^{52} N^2 O^{16}$.

Chloride of Gold and Veratrine.—A solution of veratrine in mu-

* The amount obtained is very small in proportion to the amorphous veratrine employed, so that the latter is probably a mixture of the pure base with resin; and the presence of this resin may be the reason why it is impossible, or very difficult to obtain crystals from the alcoholic solution of ordinary veratrine.

riatic acid was added to an excess of a solution of chloride of gold; the precipitate was washed with water, and after drying dissolved in alcohol, from which it separated on cooling in fine, yellow, silky crystals. These were purified by repeated crystallization from alcohol, and dried at 212° F. Analysis gave:—

	I.	II.	III.	IV.	V.	VI.		
C	41.31	41.05	..	..	..	..	64=384	41.25
H	5.97	5.91	..	..	..	..	53 53	5.69
N	..	..	..	..	..	..	2 28	3.01
O	..	..	..	..	..	..	16 128	13.75
Au	..	..	21.03	20.87	20.87	21.26	1 196.4	21.09
Cl	..	..	..	..	..	..	4 141.6	15.21

Hence the formula is $C^{64} H^{52} N^2 O^{16} HCl + AuCl^3$.

Sulphate of Veratrine.—An excess of veratrine was treated with dilute sulphuric acid; the perfectly neutral solution was filtered from the undissolved portion, and left to evaporate over sulphuric acid. When dry, the salt formed a colourless gum-like mass, which was readily triturated, and became electrical when rubbed. Dried at 212° F., it gave the following numbers:—

	I.	II.	III.	IV.			
C	59.48	59.45	..	..	64=384	59.90	
H	9.10	8.44	..	..	53 53	8.26	
N	..	..	..	..	2 28	4.38	
O	..	..	..	..	17 136	21.22	
SO ³	..	..	6.26	6.33	40 40	6.24	

From this the formula is $C^{64} H^{52} N^2 O^{16}, HOSO^3$.—Liebig's *Annalen*, xcv. p. 200.

On Butyle-mercaptan. By E. HERMANN.

Butyle-mercaptan is easily obtained by the distillation on the water-bath of a mixture of a solution of double sulphuret of hydrogen and potassium and a concentrated solution of butylosulphovinate of potash; the oily part of the distillate is deprived of water by chloride of calcium, and rectified, the portion passing between 185° and 203° F. being collected separately. Butyle-mercaptan is a colourless mobile fluid, of a disagreeable odour; its specific gravity is 0.848 at $52^{\circ}.7$ F.; it boils at $190^{\circ}.4$ F., is readily ignited, sparingly soluble in water, but miscible with alcohol and æther. Its composition is $C^8 H^{10} S^2$:—

	Found.		Calculated.
C	53.52	53.16	53.33
H	11.71	11.32	11.11
S	..	..	35.56

The density of its vapour was found to be 3.10; for a condensation of 4 vols. it was calculated 3.11.

Dilute nitric acid acts violently upon butyle-mercaptan. The

fluid is reddened by dissolving nitrous oxide; when heated, the colour disappears, and an oleaginous stratum separates.

Like other mercaptans, it forms metallic compounds. When heated with potassium, a white granular substance, $C^8 H^9 KS^2$, is produced with evolution of hydrogen, and the addition of its alcoholic solution to acetate of lead furnishes a yellow crystalline precipitate, $C^8 H^9 PbS^2$. By the gradual addition of an alcoholic solution of butyle-mercaptan to red oxide of mercury, a white substance is formed, with evolution of heat; this, when dissolved in boiling alcohol and allowed to cool, furnishes nacreous laminæ, which are fatty to the touch, and the composition of which is $C^8 H^9 HgS^2$:—

	Found.			Calculated.
C	25.78	..	..	25.39
H	5.01	..	..	4.76
Hg	..	52.22	52.88	52.91
S	..	..	..	16.94

Acetate of copper and perchloride of gold give white precipitates with butyle-mercaptan.—Poggendorff's *Annalen*, lxiv. p. 337.

On the Conversion of Toluene into Benzoic Alcohol and Toluic Acid. By M. S. CANNIZZARO.

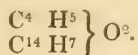
Many chemists have regarded the hydrocarbons homologous with acetene, $C^n H^{n+2}$, as the starting-point of the alcoholic series, and as the links by means of which one series is united with the other. To prove the correctness of this view, it was necessary to show that with these hydrocarbons it was possible to obtain the corresponding alcohol, and the acid $C^n H^n O^4$ of the immediately superior series; to convert acetene on the one hand into methylic alcohol, and on the other into acetic acid.

The question would have been solved if it had been proved that monochlorinated acetene is identical with chloride of methyle, for by means of the latter we may obtain in the first place methylic alcohol, and in the second cyanide of methyle or acetonitrile, which by the action of alkalies is decomposed into ammonia and acetic acid. This identity has long been admitted without experimental proof, but doubts have lately been thrown upon it, so that at present no one has succeeded in transforming any carburet, $C^n H^{n+2}$, either into alcohol, or into the acid $C^n H^n O^4$ of the superior series.

Toluene being to benzoic alcohol and toluic acid what acetene is to methylic alcohol and acetic acid, is it not possible that monochlorinated toluene would be identical with chloride of benzæthyle? and, on the other hand, if this supposition be realized, it is evident that we should be able to ascend from toluene to benzoic alcohol and toluic acid. These questions have been answered in the affirmative by experiment; thus having submitted toluene to the action of chlorine, I obtained monochlorinated toluene, $C^{14} H^7 Cl$, which not only has the composition of chloride of benzæthyle, but is iden-

tical with it, and may easily be converted either into benzoic alcohol or into toluic acid.

The toluene employed in my experiments was derived from commercial benzene by fractional distillation, and I considered the product passing between 226° and 239° F. as toluene sufficiently pure for my purpose. The monochlorinated toluene was prepared by distilling this crude toluene several times in a current of dry chlorine. The product was agitated first with a concentrated solution of potash, and afterwards with water; lastly, it was dried over chloride of calcium and distilled. By fractional distillation, and separating those portions which had a constant boiling-point, monochlorinated toluene is obtained. This body is identical with chloride of benzæthyle, not only in its elementary composition, which as given by analysis is expressed by the formula $C^{14}H^7Cl$, but also in its physical properties and reactions. Thus these two products have the same boiling-point (347° to 349° F.), and the same density in the liquid state (1.117 at 32° F.). They are also decomposed under the same conditions, and furnish identical products; thus by submitting them to the action of an alcoholic solution of potash, a mixed æther is obtained, that is to say a double oxide of æthyle and benzæthyle of the formula—



When treated with acetate of potash, they are both changed by double decomposition into chloride of potassium and acetate of benzæthyle; and the latter, when heated with an alcoholic solution of potash, is in its turn decomposed into acetic acid and benzoic alcohol.

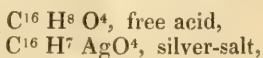
The identity of the product thus prepared with benzoic alcohol has been verified not only by analysis, which leads exactly to the formula $C^{14}H^8O^2$, but also by the comparison of the properties of these two substances. Thus when the product derived from toluene is treated with dilute nitric acid, it is converted into essential oil of bitter almonds, which I separated in a state of perfect purity by means of bisulphite of soda. It is well known that, under the same conditions, benzoic alcohol obtained by the ordinary method undergoes an exactly similar change.

The preceding statements sufficiently prove that toluene may be converted into chloride and acetate of benzæthyle, and finally into benzoic alcohol. The following experiments will prove that we may also ascend from it to the acid of the superior series, that is to say toluic acid.

For this purpose cyanide of benzæthyle is prepared by the double decomposition of monochlorinated toluene and cyanide of potassium. This is readily effected by boiling an alcoholic solution of these two bodies until no more chloride of potassium is precipitated; the liquid is then filtered and distilled to drive off the greater part of the alcohol, stopping as soon as the residue separates into two distinct strata, of which the upper one is the cyanide of benzæthyle. If this be

boiled for a long time with a concentrated solution of caustic potash, the supernatant ætherial fluid is gradually decomposed, with evolution of ammonia, and at last disappears. If the alkali be then saturated with an excess of muriatic acid, the toluic acid is precipitated in crystalline laminæ, which are more or less coloured. To purify this crude product, it is dissolved in baryta-water; the excess of base is precipitated by a current of carbonic acid, the solution of the baryta-salt is concentrated, and decomposed again by muriatic acid. The precipitate is then taken up again by æther, and the ætherial solution is evaporated.

The elementary analysis of this acid was checked by that of its silver-salt; they led to the following relations:—



formulae which are exactly identical with those of toluic acid and toluate of silver.

The acid thus prepared crystallizes in white needles, or in small nacreous laminæ. It fuses below 212° F., and distils at a higher temperature without appreciable alteration. Its vapours are as acid as those of benzoic acid. It is very soluble in alcohol and æther, slightly soluble in cold water, but much more so in hot water. Its solution reddens litmus.

The only circumstance which leaves any doubt upon my mind as to the identity of this substance with the toluic acid derived by the action of nitric acid upon cymene, is the greater fusibility of the substance just described, a property which however may perhaps arise from traces of some foreign matters. But whether they are identical or not, it is still proved by these experiments, that a hydrocarbon, such as toluene, is capable of taking up carbon and oxygen, so as to become converted into an acid of the series immediately superior, a fact which as yet has no analogue in science.—*Comptes Rendus*, October 1, 1855, p. 517.

On Igasurine. By M. DESNOIX.

The author states, that, in addition to strychnine and brucine, nux vomica contains a third base, which he calls *igasurine*. On repeatedly preparing strychnine from 100 kilogrms. of nux vomica, the author found that, after the precipitation of the strychnine and brucine by means of lime at a boiling heat, if the mother-liquors were evaporated to a certain point and left to stand, a deposition of crystals took place; and these, when dissolved in muriatic acid, decolorized with animal charcoal, and precipitated by ammonia, furnished the new base in the form of a yellowish powder, which was at first amorphous, but afterwards became crystalline. By repeating this treatment with the substance dissolved in alcohol, it was obtained pure.

Igasurine forms white silky prisms, containing about 10 per cent. of water of crystallization, and possessing a strong bitter taste. It

is distinguished from brucine by its degree of solubility. The latter requires 500 parts of boiling water for its solution, and crystallizes therefrom very slowly, whilst igasurine dissolves in 200 parts of water, and crystallizes very rapidly on cooling. In the presence of tartaric acid igasurine is thrown down by the alkaline bicarbonates, but this is not the case with brucine. All the other reactions, even to the behaviour in polarized light, are exactly like those of brucine. —*Journ. de Pharm.*, xxv. p. 202.

On some new Compounds of Chloride of Cadmium.
By KARL VON HAUER.

We are acquainted with a large series of chlorides of the heavy metals which form double salts with the chlorides of ammonium and potassium. The number of those which enter into combination with chloride of sodium is more limited. We are also acquainted with a small number which furnish double salts with chloride of barium and the other chlorides of the electro-positive series. These chlorides, and their best-known double compounds with the chlorides of barium, strontium, calcium and magnesium, are as follows:—

Antimony, SbCl ³ .	2BaCl + SbCl ³ + 5HO (according to Poggiale, similar compounds may be obtained with strontium, calcium and magnesium).
Tin, SnCl SnCl ² .	BaCl + SnCl + 4HO BaCl + SnCl ² + 5HO SrCl + SnCl ² + 4HO MgCl + SnCl ² + 5HO
Mercury, HgCl.	BaCl + 2HgCl + 2HO Chloride of mercury and strontium (Bonnsdorff). CaCl + 2HgCl + 6HO CaCl + 5HgCl + 8HO MgCl + HgCl + 6HO MgCl + 3HgCl + 5HO
Gold, AuCl ³ .	Terchloride of gold and barium (Bonnsdorff). Terchloride of gold and strontium (Bonnsdorff). CaCl + AuCl ³ + 6HO MgCl + AuCl ³ + 12HO
Platinum, PtCl ² .	BaCl + PtCl ² + 4HO SrCl + PtCl ² + 8HO CaCl + PtCl ² + 8HO MgCl + PtCl ² + 6HO
Palladium.	Chloride of palladium and barium. Chloride of palladium and calcium. Chloride of palladium and magnesium (Bonnsdorff).

No notice is here taken of the compounds prepared by the agency

of galvanism by Becquerel, as nothing further is known of them, and they may possess a different character from the above-mentioned salts.

From the above, it appears that all the chlorides referred to are capable of entering into other double combinations besides the double salt with barium. The barium compound thus appears to form a definite limit; if this cannot be prepared, the chloride employed cannot form any other double compounds, except those with the alkaline chlorides. If, on the contrary, the chloride of a metal forms a double compound with chloride of barium, it may actually play the part of an acid, and then of course form other double salts with similar chlorides. That this faculty is not confined to the higher chlorides is shown by tin, the protochloride of which forms such compounds. The compounds of palladium also appear to be of a similar nature.

As the author had some time since prepared a double compound of chloride of cadmium with chloride of barium, a salt which was characterized by its great power of crystallization, it became interesting to try whether, like the metals already referred to, cadmium was not also capable of forming other double compounds with basic metallic chlorides. The result of the experiments made justified the supposition just expressed. The author succeeded in preparing numerous double salts of chloride of cadmium with the chlorides of strontium, calcium, magnesium, manganese, &c.

As the monochloride of cadmium is the only chloride of this metal at present known, these salts must for the present be arranged with those formed with protochloride of tin. Nevertheless it is very probable that a protochloride of cadmium (sesquichloride of cadmium) may be prepared, and that the present chloride of cadmium, like the monochloride of mercury, represents a higher compound of chlorine. For it appears, from the summary given at the commencement, that protochloride of tin is the only low chlorine compound which forms double salts of this description; and this acquires still greater probability, as there is a protoxide of cadmium (suboxide, Cd^2O), which was obtained by Marchand, by the calcination of the oxalate in the absence of the atmospheric air.

The name of *chlorocadmiates* appears to be generally applicable to the recently-prepared double compounds of chloride of cadmium, as well as to a number of compounds with the alkaline chlorides previously described by the author; for the very existence of this considerable number of salts proves that chloride of cadmium presents the character of an electro-negative constituent in a remarkable degree.

From their chemical constitution, these salts may be divided into three readily-distinguishable groups, according as the chloride of cadmium forms basic, neutral, and acid or sub-, mono- and bi-acid salts. For these three groups, therefore, the following denominations may be adopted:—I. Chlorosesquicadmiates; II. chloromonocadmiates; and III. chlorobicadmiates.

The *chlorosesquicadmiates*, in which 2 atoms of the basic chloride

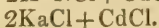
are combined with 1 atom of chloride of cadmium, correspond with the general formula,—



in which R=ammonium, potassium, &c.

These salts cannot generally be prepared by the evaporation of a solution containing the two compounds mixed in a proportion corresponding with the formula; they usually require for their formation a great excess of the basic chloride.

Of the salts previously described by the author, this group includes the two anhydrous compounds of ammonium and potassium, the composition of which was found to agree with the formulæ

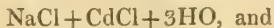


When the salts of this group are dissolved in water, they are generally decomposed, and cannot be recrystallized. Thus first of all a bicadmiate crystallizes; and it is only after the removal of this, and further evaporation of the mother-liquor, that a small quantity of the sesquicadmiate is reproduced. The salts of this section generally form large crystals.

The *chloromonocadmiates*, in which the two chlorides occur in equal atomic proportions, agree in composition with the formula



The salts belonging to this group are very few. Of those described in the author's previous paper, it includes the two compounds with sodium and barium, the composition of which is expressed by the formulæ



The rarity of the salts belonging to this group rendered it at first rather difficult to find the salts hereafter to be described. It was necessary to try many combinations before the compounds which it is possible to obtain could be discovered.

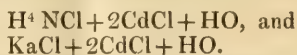
The *chlorobicadmiates*, lastly, in which 2 atoms of the electro-negative constituent combine with 1 atom of the base, agree with the general formula,—



The salts belonging to this group are numerous. Some of them crystallize when the chlorides composing them are mixed in almost any proportions. Thus if the proportions of a monocadmiate are realized, a bicadmiate is almost always produced first by the spontaneous evaporation of the fluid, and after the removal of this the mother-liquor furnishes a sesquicadmiate in abundance. On the other hand, several salts of this group require for their formation the presence of a great excess of chloride of cadmium in the solution. These are generally the combinations of chloride of cadmium with metallic chlorides, which are also capable of forming monocadmiates. With these the monocadmiate obstinately crystallizes first, and it is only when a great excess of chloride of cadmium remains that the

bicadmiate crystallizes. The salts of this group, with the exception of those just referred to, may be recrystallized without decomposition.

Of the salts formerly described by the author, this group includes the two following compounds of ammonium and potassium:—



The series of the chlorocadmiates is distinguished by the great facility of crystallization possessed by the salts belonging to it, with but few exceptions. Most of them may be easily obtained in crystals of considerable size. This is a character which is generally very prominent in the salts of cadmium, and the compounds of this metal furnish some of the finest crystals that can be prepared artificially.

The above-mentioned salts are generally colourless and transparent, with brilliant faces. When however the basic chloride is coloured, the crystals exhibit the colour of this. With the exception of the calcium-salts, which are deliquescent, most of them are tolerably permanent in the air. A few effloresce in dry air.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xvi. p. 409.

Note on various Phenomena of Oxygenation. By F. KUHLMANN.

New Process of Formation of Sulphuric Acid.

It is well known that many hydrocarbons become resinified by contact with the air, in consequence of an absorption of oxygen. This is the case with most of the essential oils, and the drying oils undergo analogous modifications by a slow acidification; but it has not been suspected that these hydrocarbons, before undergoing any considerable modification in their constitution and properties, form, as it were, a provision of oxygen under such conditions, that when they come in contact with bodies which have the property of more immediately forming an intimate combination with oxygen, they yield the absorbed oxygen to the latter, and again acquire their original state, becoming again capable of attracting oxygen from the air. In these cases the resinifiable essential oils constitute sources of oxygen for the benefit of other bodies, and to a certain extent play the part taken by deutoxide of nitrogen in the manufacture of sulphuric acid.

When oil of turpentine is exposed to the air for a few days, and then agitated with a solution of sulphurous acid in water, the mixture becomes strongly heated, the temperature rises to 122° F., and even higher, and the sulphurous odour soon disappears, leaving only that of the turpentine. In this reaction, which appears to be facilitated by the solar radiation, formation of sulphuric acid takes place at the expense of the oxygen absorbed by the turpentine, which is taken from it by the sulphurous acid before it has time to appropriate it in a more permanent manner.

If sulphurous acid gas be passed into a moist glass globe containing the vapour of an oxygenated essential oil, the sulphurous

acid disappears by degrees; on the other hand, if a mixture of an aqueous solution of sulphurous acid and an aërated essential oil be allowed to become concentrated in contact with the air, the sulphuric acid formed carbonizes the essential oil without the necessity of raising the temperature of the mixture.

The oxygenating action of the aërated essential oil is not confined to sulphurous acid; it extends also to other acids, such as hyposulphurous acid, the sulphites, arsenious acid, &c.

Peculiar Reactions of the Essential Oils in Painting.

The essential oils, from the nature of their constituent principles, may be regarded as possessing naturally, and especially under the influence of heat or of the sun, a reductive power which acts slowly upon white lead and the coloured oxides. However this may be, the resinifiable essential oils temporarily possess another property of an opposite nature, as I have just shown; and this deserves to be taken into consideration in the study of the modifications undergone by paintings in oil, namely, that of absorbing oxygen by mere contact with the air. The result of this is, that at the moment of their employment the essential oils may exercise an oxidizing action, tending to destroy vegetable colours and to modify some mineral colours. Thus

Litharge, heated with aërated oil of turpentine, furnishes the puce-coloured oxide of lead.

If oil of turpentine be agitated at the ordinary temperature with the hydrated protoxides of iron, tin and manganese, these oxides pass to a higher degree of oxidation. With a solution of protosulphate of iron, basic sesquisulphate is produced, which separates from the liquid. The white precipitate formed by ferrocyanide of potassium with a protosalt of iron immediately acquires the intense colour of prussian blue.

Blue and red flowers, decolorized by sulphurous acid, reacquire their colours by contact with the aërated essential oil. The essential oil, freshly distilled, possesses no oxidizing power.

In the association of colours applicable to painting in oil, regard must therefore be had not only to the modifications which may be produced upon certain colours by the various mutual reactions of the colouring matters, but also to the oxidizing action of the essential oil, which must be manifested at the first moment of its application in the form of varnish.

General Considerations.

In all the reactions just referred to, the oil of turpentine, and in general the essences which are capable of absorbing oxygen from the air, behave as oxidants, the energy of which is sufficiently marked by the great elevation of temperature produced by the contact of the aërated essential oil with a solution of sulphurous acid.

It is important to ascertain whether this oxidizing property belongs to certain oils, and whether the proof of this fact may not account for the frequent spontaneous combustion of oiled tissues. Con-

siderable interest also attaches to the investigation of the action of the vapours of essential oils upon putrid miasmata, and the determination of the question whether, in these cases, there is not a combustion of the principles diffused in the air.

If oxygen can thus dissolve in certain liquids without combining, we are led to suppose that where it is disengaged it exerts its action upon the bodies with which it is in contact in the dissolved state before becoming gaseous. Are not the same circumstances presented in all the chemical reactions in which in our explanations we have recourse to the intervention of nascent gases?

Thus we shall be led to inquire whether other bodies do not share with certain essences in the power of forming a provision of oxygen, and yielding this reagent to assist in various reactions. This study may throw great light upon the phenomena of animal and vegetable physiology. The solution of oxygen in the blood by the act of respiration, and its subsequent assimilation, already present a great analogy to the phenomena which have just been described. As a question of health, it would be advisable to ascertain what may be the consequences of the respiration of air charged with essential oil in apartments newly varnished. On the other hand, we know how unfit water which has not been aerated is for good alimentation.—*Comptes Rendus*, Sept. 24, 1855, p. 470.

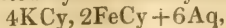
On a peculiar Behaviour of fused Bismuth. By R. SCHNEIDER.

It is generally regarded as a certain proof of the expansion which bismuth undergoes in solidification, that when that metal is fused and poured upon a cold plate, numerous globules of bismuth are thrown up during its solidification. This proof is not just; at least, chemically pure bismuth does not exhibit the projection of globules during solidification, whatever expansion may take place. This phenomenon is perhaps only observed with impure bismuth, and it is remarkable that the globules of bismuth thrown up from this during solidification possess a high degree of purity; even when the metal employed contains foreign bodies, such as sulphur, arsenic, iron, nickel, copper and silver, in considerable quantities, as much as 50 per cent. of globules have been thrown up, in which there was always more than 99.5 per cent. of bismuth. It is worthy of remark, that of the heavy metals only silver accompanies the bismuth thrown up, whilst the copper remains entirely in the general mass.

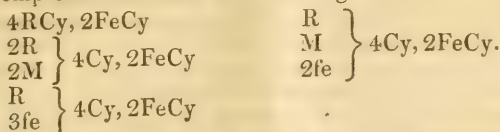
No doubt the protrusion of the bismuth-globules from the surface of the impure metal is caused by the expansion of the binary compounds of the bismuth with its impurities at the moment of their solidification; the bismuth, which remains fluid in consequence of its lower melting-point, being thus pressed out of the mass. As at the moment of this protrusion these foreign bodies are already solid, they cannot of course accompany the bismuth. The author believes that this property might be employed advantageously, at all events for a preliminary purification of commercial bismuth.—*Bericht der Akad. der Wiss. zu Berlin*, 1855, p. 495.

On some Double Cyanides. By F. REINDEL.

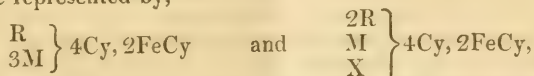
All the double protocyanides which have hitherto been prepared, and which are represented by the ferrocyanide of potassium,



may be comprehended under the following formulæ:—

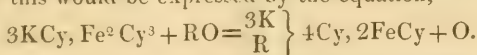


The author set himself the task to prepare compounds which should be represented by,—



in which R, M, and X represent metals of the alkalies and alkaline earths.

The basis for the preparation of double cyanides of this nature was derived from the well-known reaction between ferridcyanide of potassium in the presence of a reducing agent. From this the question necessarily arose, whether it is not possible, by the employment of other bases and a powerful reducing agent, such as grape-sugar, to obtain ferrocyanide of potassium, in which a portion of the potassium may be replaced by ammonium, sodium, &c. The production of this would be expressed by the equation,—



In this manner, in fact, corresponding protocyanides may be obtained from nearly all the double cyanides, which agree with the formula of the ferridcyanide of potassium. The following are some of those which have been analysed:—

Ferrocyanide of Potassium and Ammonium, $\begin{array}{l} 3\text{K} \\ \text{NH}_4 \end{array} \left. \vphantom{\begin{array}{l} 3\text{K} \\ \text{NH}_4 \end{array}} \right\} 4\text{Cy}, 2\text{FeCy}$

+ 6Aq.—When ammonia is poured over powdered ferridcyanide of potassium with grape-sugar (in the proportion of 20 : 1), and the fluid is left for several days, with frequent shaking, its colour, which is at first dark, gradually passes to a paler tint, which in the course of eight or ten days becomes pure yellow. In most cases, when large quantities are employed, yellow crystals are soon deposited. The stopper of the bottle must not be inserted too firmly, as otherwise the gaseous products of the oxidation of the grape-sugar may easily burst it. An excess of ammonia has no injurious action, and a constant product is always obtained. Although the pure product may be evaporated to the point of crystallization without decomposition, this behaviour is changed in the presence of undecomposed grape-sugar and ammonia; it is therefore the best plan, in order to free the salt at once, as far as possible, from the accompanying products of oxidation, to precipitate it with alcohol, and then recrystallize it repeatedly from water.

In this way pale yellow square prisms are obtained; they dissolve readily in cold, and still more so in hot water; they are partially decomposed even at temperatures between 176° and 212° F., and at a higher temperature evolve hydrocyanic acid and cyanide of ammonium. The precipitates with metallic solutions are exactly the same as when ordinary ferrocyanide of potassium is employed; when heated with potash, soda, &c., ammonia is evolved, and the corresponding protocyanides are formed.

In the analysis of these compounds two different methods were adopted for the determination of the alkalies. As the author had ascertained by experiment that the cyanogen in ferrocyanide of potassium could be determined pretty exactly in the form of ferrocyanide of copper, so that a complete decomposition of the double cyanide takes place, the substance to be analysed was, in the one case, precipitated whilst boiling with an excess of chloride of copper; the copper was thrown down from the filtrate by sulphuretted hydrogen, the fluid was filtered and evaporated on the water-bath, and the potassium and ammonium determined in the usual way by chloride of platinum. In the second method, the decomposition of the cyanide was effected in the way recommended by Bolley, by calcination with a mixture of sulphate and nitrate of ammonia; the residue was digested with caustic ammonia to separate the oxide of iron, filtered, evaporated and weighed.

The analysis furnished the following results:—

	Found.		Calculated.
K	29.58	} 86.87	29.28
NH ⁴	4.65		4.48
Fe	13.87		13.94
Cy	38.77		38.85
HO	13.13		13.45

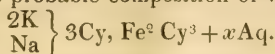
Ferrocyanide of Potassium and Sodium, $\left. \begin{smallmatrix} 3\text{K} \\ \text{Na} \end{smallmatrix} \right\} 4\text{Cy}, 2\text{FeCy} + 7\text{Aq}$, is obtained by treating ferridcyanide of potassium and grape-sugar with caustic soda, or by treating the latter with a solution of the preceeding salt. For the separation and purification of this compound, alcohol is also employed as a precipitant. The salt is obtained in the form of vitreous rhombic prisms, which approach pretty closely to the square form; they do not effloresce, and are readily soluble both in hot and cold water. They only lose their water of crystallization at a temperature below 392° F. Analysis gave,—

	Found.	Calculated.
K	28.18	28.29
Na	5.34	5.55
Fe	13.56	13.47
Cy	37.75	37.54
HO	15.14	15.15

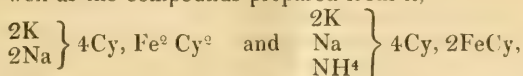
The conversion of the double ferridcyanides into double ferrocyanides always takes place with much more ease by the employment of alkaline sulphites. Nevertheless in these cases grape-sugar

is to be preferred as a reducing agent, because the separation of the alkaline sulphates presents such great difficulties.

If chlorine gas be passed through a solution of the ferrocyanide of potassium and sodium, chloride of potassium is separated, and a salt is produced, the probable composition of which is,—



This, as well as the compounds prepared from it,



will be further investigated.

The author has also occupied himself with the derivatives of ferridecyanide of sodium. This salt, when crystallized at the ordinary temperature of the air, forms, as stated by Bette, ruby-red (quadratic?) prisms, with truncated lateral edges. It does not deliquesce, but becomes covered gradually with a yellow powder and effloresces. This loss of water takes place very gradually.—*Journ. für Prakt. Chem.*, lxx. p. 450.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Glasgow, September 12th, 1855.

On the Composition of the Iron Ores called Brass occurring in the Coal-Measures of South Wales. By E. CHAMBERS NICHOLSON and DAVID S. PRICE, PH.D., F.C.S.

THERE are three kinds of ores to which the name brass is applied; they are considered to be an inferior class of ore, and are even rejected by some iron-masters. One is compact, heavy and black, from the admixture of coaly matter, and exhibits, when broken, a coarsely pisiform fracture. A second is compact and crystalline, not unlike the darkest-coloured mountain limestone of South Wales in appearance. The third is similar in structure to the first-named variety; the granules, consisting of iron pyrites, are mixed with coaly matter, and cemented together by a mineral substance, similar in composition to the foregoing ores. It is from the yellow colour of this variety that the name *brass* has been assigned to the ores by the miners.

The ores have respectively the following composition:—

	I.	II.
Carbonate of iron	68·71	59·73
Carbonate of manganese	0·42	0·37
Carbonate of lime	9·36	11·80
Carbonate of magnesia	11·80	15·55
Iron pyrites	0·22	trace
Phosphoric acid	0·17	0·23
Coaly matter	8·87	9·80
Clay	..	2·70
	99·55	100·18

III.	
Carbonate of iron	17·74
Carbonate of lime	14·19
Carbonate of magnesia	12·06
Coaly matter	6·10
Iron pyrites	49·72
Phosphoric acid	trace
	99·81

It is unnecessary to allude to the third variety; as an iron-making material, its colour admits of its being at all times separated from the others. The pyrites which it contains, we may remark, is bisulphuret of iron.

It is to the ores I. and II. that we would direct attention. The reason of their having hitherto been comparatively disregarded may be attributed, either to their having been mistaken for the so-called brass of coal, or to their being difficult to work in the blast-furnace in the ordinary manner, through the belief that they were similar in constitution to the argillaceous ores of the district. It will be seen from the above analyses, that they are varieties of spathic iron ore, in which the manganese has been replaced by other bases. If treated judiciously, they would smelt with facility, and afford an iron equal to that produced from the argillaceous ores. From the large amount of lime and magnesia which they contain, their employment must be advantageous in an œconomic point of view.

An interesting feature in these ores is their fusibility during calcination on the large scale. When this process is conducted in heaps, the centre portions are invariably melted. This, considering the almost entire absence of silica, is apparently an unexpected result. The fused mass is entirely magnetic and crystalline. Treated with acids, it dissolves with great evolution of heat.

The following is its composition:—

Protoxide of iron	38·28
Sesquioxide of iron	32·50
Protoxide of manganese	0·38
Lime	12·84
Magnesia	13·87
Phosphoric acid	0·17
Sulphur	0·23
Silicic acid	1·20
Alumina	0·51
	100·08

From the above analysis, it is probable that the fusibility of the compound is owing to the magnetic oxide of iron acting the part of an acid. When thoroughly calcined and unfused, the ores retain their original form; and if exposed to the air for any length of time, crumble to powder, from the absorption of water by the alkaline earths.—*Communicated by the Authors.*

THE CHEMICAL GAZETTE.

No. CCCXV.—December 1, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Cyanides of Platinum. By A. SCHAFARIK.

THE author's intention was to complete the two series of proto-cyanides of platinum described by Knop and Schnedermann, and therefore to prepare the compounds corresponding to the copper-coloured platino sesquicyanides of ammonium and potassium, and the cyanide of platinum.

In testing the methods for the preparation of Gmelin's salt, the author, after repeated comparison of the different known methods, has fallen back upon that recommended by Knop, which he regards as the most convenient, as by its means large quantities of the salt may be prepared. As regards the composition of the salt thus prepared, Quadrat has stated that it is somewhat different from that of Gmelin's salt, with which Knop considered it to be identical. This assertion of Quadrat has, as is well known, been contradicted by other chemists, whose opinion is supported by the author.

Protocyanide of Platinum and Sodium, $\text{PtCy}^2\text{Na} + 3\text{HO}$.—Protocyanide of platinum and barium (prepared according to Quadrat's method) was dissolved in a little hot water, and mixed with an excess of sulphate of soda; 10 times its volume of a mixture of equal parts of æther and alcohol was then added, and the whole was filtered after standing for several hours. The clear solution, when evaporated first in the air and afterwards *in vacuo* over sulphuric acid, became entirely converted into beautiful, colourless, brilliant, glassy prisms, of about 8 millims. in length and 1 millim. in thickness. Analysis:—

Calculated according to Quadrat, $\text{Pt}^5\text{Cy}^{11}\text{Na}^6 + 28\text{HO}$.					
Pt	48·62	1 = 99	49·25	495	42·27
Cy	..	2 52	..	286	
Na	11·58	1 23	11·44	138	11·78
Aq	13·85	3 27	13·43	252	21·50

Protocyanide of Platinum and Ammonium, $\text{NH}^4\text{PtCy}^2 + \text{HO}$.—This salt was prepared by Quadrat, by mixing protocyanide of platinum and potassium with an excess of sulphate of ammonia, *eva-*
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porating the mixed solution, and extracting the dry mass with a mixture of æther and alcohol. It may also be obtained by dissolving protoeyanide of platinum and barium, and precipitating it with a mixture of caustic ammonia and carbonate of ammonia; the filtrate, when slowly evaporated, is entirely converted into beautiful crystals. The latter method is preferable, because from its great crystallizability the barium-salt is very easily obtained perfectly pure; in Quadrat's method traces of salts of potassium may always be retained. Nevertheless both methods furnish a preparation of equal purity, consisting of thin, deep, citron-yellow prisms, of 50 to 80 millims. in length, which generally diverge in a radiate form, and exhibit in a high degree that splendid blue fluorescence at the surface, which is peculiar to the yellow salts of this group. For its solution the salt requires a quantity of cold water about equal to its weight, and a still smaller quantity of alcohol; it is therefore only crystallizable after evaporation. When very concentrated solutions of this salt, mixed with caustic ammonia, are evaporated on the water-bath, colourless transparent needles are formed in them; these have the same beautiful azure-blue lustre as the yellow salt. As soon as they are taken out of the fluid they become yellow. Knop, who first observed this phenomenon, explains it by loss of water, and is therefore of opinion that the white crystals contain more water than the yellow ones; Quadrat, on the other hand, thinks that the yellow colour is caused by a loss of ammonia; and this view is apparently supported by the circumstance observed by him, that the crystals which have become yellow in the air, again become white in an atmosphere of ammonia; this is also the case with crystals which were originally yellow. The author has however discovered another circumstance, namely, that if a weighed portion of fresh, shining yellow, transparent crystals be put under a bell-glass with caustic lime upon which caustic ammonia is dropped, they will soon become pure white, but turbid, and although perfectly dry, they are found to undergo a considerable loss of weight (4 to 5 per cent.). This fact evidently confirms Knop's explanation. If these white crystals be now exposed to the air, they again become yellow, although slowly; but if they be placed over sulphuric acid, they remain white. The latter circumstance evidently excludes Quadrat's explanation, for ammonia would certainly be lost more readily over sulphuric acid than by simple exposure to the air. From this it appears that the yellow transparent salt is $\text{PtCy}^2(\text{NH}^4) + 2\text{Aq}$; and that the white salt which crystallizes from saturated ammoniacal solutions, and into which the yellow crystals are converted by exposure to an atmosphere of ammonia, is $\text{PtCy}^2(\text{NH}^4) + \text{Aq}$. That the yellow salt, when in an atmosphere of ammonia, instead of taking up water, gives off that fluid, is shown by the loss of weight and the turbidity; the abstraction of water is evidently the result of the powerful affinity of the dry ammonia for water. In the air, the salt deprived of half its water by ammonia of course again attracts its second atom of water and becomes yellow; this however cannot take place over sulphuric acid, and it therefore remains white. At 212°F . both salts lose their water, but

not entirely; this only takes place at about 302° F., when they are milk-white or pearly. When the salt acquires a brown colour by drying, as stated by Quadrat and observed also by the author, this is to be attributed to the impurities of the æther and absolute alcohol. The pure salt, as already stated, is of a beautiful milk-white; and when it is dissolved in this condition in absolute alcohol, and the solution is evaporated *in vacuo* over sulphuric acid, crusts of radiate colourless needles shoot from the margin of the vessel, which at last coat the whole vessel with a network, and exhibit a beautiful violet fluorescence; they become yellow very rapidly when exposed to the air. Whether these crystals are anhydrous proto-cyanide of platinum and ammonium, or merely the white salt, $\text{PtCy}^2(\text{NH}^4) + \text{Aq}$, which is produced from the yellow crystals by the vapour of ammonia, could not be decided from the data above given. Analysis gave:—

	Calculated, NH^4PtCy^2 .	Found.	Calculated, $(\text{NH}^4)^6\text{Pt}^5\text{Cy}^{11}$.
Pt	= 99 58.58	58.05 58.88	495 55.68
Cy^2	= 52 30.77		286 32.17
NH^4	= 18 10.65		108 12.15

	Calculated, $\text{NH}^4\text{PtCy}^2 + \text{Aq}$.	Found.	Calculated, $\text{NH}^4\text{PtCy}^2 + 2\text{Aq}$.	Found.
Pt	= 99 55.62	55.88	99 52.94	52.22
Cy^2	= 54 ..	..	52	
NH^4	= 18 ..	..	18	
Aq	= 9 5.01	5.10	18 9.63	10.05

Protocyanide of Platinum and Barium.—The author has prepared this salt, which was discovered by Quadrat, in various ways. Its composition was always $\text{PtCy}^2\text{Ba} + 2\text{HO}$.

As this salt crystallizes more readily than any of the other similar salts (according to Quadrat it requires 33 parts of water at 61° F. for its solution), it serves best for preparing the other salts quickly and in a state of purity, by the precipitation of a weighed quantity of it with an equivalent quantity of the sulphate or carbonate of the required base, and setting the filtrate to crystallize. In this way the author has always obtained solutions, which, when evaporated to the last drop, still gave pure salts. But there is one troublesome part in the preparation of the barium-salt, namely, the complete washing of the protocyanide of platinum and copper, which, even with moderate quantities (over 100 grms.), takes a week, in consequence of the slimy consistency of that product. Decantation is of no use, as the body in question is completely deposited only from saline solutions, but remains for the most part suspended in pure water.

The author has prepared the barium compound in a very short time, and perfectly pure, directly from the protocyanide of platinum and potassium, in the following manner:—The potassium-salt is

dissolved in as little cold (or moderately warm) water as possible; an equivalent quantity of pure sulphuric acid (23 parts of hydrated acid to 100 parts of the salt) is added, taking care to avoid over-heating, which would separate protocyanide of platinum, and afterwards 10 times the volume of strong alcohol (0.863 sp. gr.). The addition of a little æther facilitates the precipitation of the sulphate of potash. The mixture is placed in cold water for some hours, when the sulphate of potash is almost entirely deposited; the filtered fluid is then evaporated to one-third, mixed with water, and saturated whilst boiling with carbonate of baryta. The product is perfectly pure, as the traces of the salt of potash which are taken up by the alcohol remain entirely in the mother-liquor. Quadrat had noticed that the treatment of protocyanide of platinum and potassium with alcohol and sulphuric acid, furnished brick-red, deliquescent needles, but without recognizing them as cyanide of platinum.

Protocyanide of Platinum and Strontium, $\text{SrPtCy}^2 + 2\text{HO} + 3\text{Aq}$. — This salt, when prepared by saturating pure hydrocyanide of platinum with carbonate of strontia at a boiling heat and evaporating *in vacuo*, forms large crystals of a milk-white colour *in vacuo*, but which, when exposed to the air, soon acquired a delicate violet tint throughout. By a second preparation, in much larger quantity, but with hydrocyanide of platinum which was not quite pure, a mass of crystals was obtained of a more prismatic form and a yellowish colour, but with a milky violet fluorescence in the axial direction. These crystals evidently contained a small quantity of sulphocyanide of strontium, as, when precipitated with sulphate of magnesia containing iron, they acquired a light blood-red colour in course of time. From their mother-liquor in the exsiccator, numerous colourless transparent crystals were produced; these exhibited a beautiful reddish-violet fluorescence in the direction of their axis, and in their form exactly resembled the usual arragonite combination (prism, dome and vertical pinakoid); they are therefore orthorhombic. Pure protocyanide of platinum and strontium is consequently quite clear, and that it should generally have occurred to the author in turbid crystals, is not more remarkable than the occurrence of the same phænomenon (of crystals sometimes limpid, sometimes turbid) in so many other salts.

The salt was also prepared by boiling protocyanide of platinum and copper (prepared from protocyanide of platinum and potassium and sulphate of copper) with strontian water; white, nacreous laminæ were obtained (as from the percyanides). But in the latter case a crust of indistinct yellow crystals is formed all round, which, however, when laid on paper over night, become white, so that the author could not determine whether the yellow salt contained more or less water than the white. Probably the slight excess of strontia which remains in the last case, even when carbonic acid is employed, may favour the production of another hydrate.

The beautiful milky or transparent crystals, prepared by all these methods, when left in the exsiccator over sulphuric acid for twenty-

four hours, acquire a splendid purple-violet colour, like a solution of permanganate of potash, and at the same time a golden-green, metallic, superficial lustre; this change is however only superficial, as when exposed to the air the crystals completely regain their previous appearance in a few days. A solution of the salt, also, when swung round in hot vessels, coats them with a violet-purple crust, with a golden-green lustre. No doubt this colour corresponds with a peculiar stage of hydration, and with a sufficiency of material and time this hydrate might be obtained in crystals; the author proposes hereafter at least to determine the amount of water in the purple salt. At 212° F. the salt becomes turbid throughout, and acquires a deep orange colour, deeper than that of the dry barium-salt; at the same time the golden-green surface-lustre is converted into azure. At 302° F. the salt becomes white and anhydrous, but, like the barium-salt under the same circumstances, it is so sensitive to moisture, that when breathed upon it immediately acquires a blackish-purple colour. Analysis gave:—

										SrPtCy ² +2HO+3Aq.	
Pt	40.85	40.73	..	..	..	..	1	=99	41.25		
Cy	..	..	..	..	..	..	1	52			
Sr	18.26	18.43	..	..	..	..	1	44	18.33		
HO	8.16	} 19.84	} 7.89	} 19.68	} 7.08	} 19.99	2	18	7.50	} 18.75	
Aq	11.68										

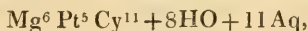
Protocyanide of Platinum and Calcium has the formula CaPtCy²+2HO+3Aq, corresponding with that of the strontium-salt.

Protocyanide of Platinum and Magnesium.—Pure crystallized protocyanide of platinum and barium was dissolved in water, and precipitated by an excess of sulphate of magnesia; the clear fluid was then evaporated, and the residue extracted with absolute alcohol mixed with a little æther. The extract was evaporated, the residue dissolved in water, the solution filtered, and evaporated *in vacuo* over sulphuric acid. The author obtained the well-known beautiful crystalline crusts, with crystals of 2 to 4 millims. in thickness. The saturation of cyanide of platinum with carbonate of magnesia at a boiling heat gives exactly the same product as the precipitation of protocyanide of platinum and barium with sulphate of magnesia, or the evaporation of protocyanide of platinum and potassium with sulphate of magnesia and extraction with alcohol; the author indeed did not analyse the compound, but upon theoretical grounds, as well as from its appearance and behaviour, there can be no doubt upon the subject. Quadrat found that the salt thus formed was of a paler red than that prepared according to his process, or almost of a rose-colour; the author, on the contrary, found that all its tints were deeper; the bright golden-green of Quadrat's salt in particular was dark metallic greenish blue in the product from cyanide of platinum.

If the salt, deprived of water, be dissolved in hot absolute alcohol, of which it requires a considerable quantity, on cooling the whole fluid is filled with a tissue of delicate, white, satiny, filamentous crystals; the access of air causes them soon to become yellow, and

at last they contract into crystalline crusts of a carmine-red colour, with a golden lustre. If the dry salt be dissolved in such a quantity of alcohol that on cooling no crystallization takes place, and the solution be allowed to evaporate in a shallow dish in warm dry air, thin citron-yellow tables, or rather laminæ, with a fine blue superficial fluorescence, are obtained; these are rectangular, and characteristically grouped in a fan-like form. These citron-yellow bundles of laminæ evidently correspond with those yellow masses into which the red salt is converted at a temperature of 86° to 104° F., whilst the asbestos-like needles are $\text{MgPtCy}^2 + 2\text{HO}$, the same salt into which the red crystals are converted at a temperature of 212° F.

Quadrat found in his salt 18.69 per cent. of water of crystallization (escaping at 212° F.), and 14.57 per cent. of hydrate-water (which only disappears at a high temperature), or together the large amount of 33.26 per cent. of water. At the same time, however, he gives the formula—



which only represents 16.70 per cent. of water, but requires 48.34 per cent. of platinum, or 5 per cent. more than the reality. To obtain 33 per cent. of water, the formula must be taken as $\text{Pt}^5 \text{Cy}^{11} \text{Mg}^6 + 47\text{HO}$, which gives 33.15 per cent. of water, but only 38.80 per cent. of platinum, which is 5 per cent. too little. The author's analyses gave,—

Calculated, $\text{MgPtCy}^2 + 2\text{HO} + 5\text{Aq}.$		Found.		Calculated, $\text{MgPtCy}^2 + 6\text{HO}.$	
Pt 99 = 43.81		43.48	43.96	43.37	99 = 45.62
Cy 52 23.01		5.79	5.53	5.36	52 23.96
Mg 12 5.31		7.05	6.45	8.29	12 5.53
HO 18 7.96	} 27.87	} 25.30	} 24.93	.. 18	8.30
Aq 45 19.91				18.45	36 16.59

The determinations of the platinum and magnesium agree with the first formula, but the amounts of water are too small; but if the quantities of platinum and magnesium be reduced to a constant quantity of anhydrous salt, we find,—

Calculated, $\text{MgPtCy}^2.$		Found.			Calculated, $\text{Mg}^6 \text{Pt}^5 \text{Cy}^{11}.$	
Pt 99 = 60.74		58.21	58.56	58.89	495 = 58.03	
Cy 52 31.90		..	..	..	286	33.53
Mg 12 7.36		7.75	7.46	7.28	72	8.44

The amount of magnesium agrees well with the first formula, but that of platinum always differs from it, and even approaches that of the complicated formula. The author is unable to discover the error either in his methods or in his operations; he proposes to repeat his experiments in order to ascertain the cause of this difference. However, the derivation from a salt, which has the consti-

tution $\text{BaPtCy}^2 + 4\text{HO}$, sufficiently shows that the formula of the magnesium-salt can be no other than that already given; and Baumert has made two analyses of the anhydrous salt, prepared according to Quadrat's method, which gave 60.51—59.81 Pt, and 7.38—7.28 Mg.

Protocyanide of Platinum and Copper, CuPtCy^2 .—This is produced whenever a solution of a protocyanide of platinum compound is mixed with a solution of a copper-salt; it forms a voluminous, bluish-green, or yellowish-green precipitate, which is completely deposited from a fluid containing an excess of the copper-salt within twenty-four hours, but when washed by decantation with pure water, always remains partially suspended in that fluid. We must therefore have recourse to filtration; but this process will last a week even with moderate quantities, as the precipitate is perhaps worse than hydrate of alumina for forming a gelatinous stratum upon the paper. When dried, it shrinks together remarkably, breaks up, and becomes converted into shining, sharp-edged fragments of a deep-grass or leek-green colour, which however when pounded furnish a dull light green powder. The salt retains humidity obstinately, like all the double metallic protocyanides, and for the purpose of analysis it must be dried at 302° to 356° F. When heated to redness in closed vessels, it acquires a deeper green colour, and then becomes brown with loss of cyanogen, which as it goes off burns with a beautiful purple flame bordered with yellow. The gas evolved has an extremely penetrating and powerful odour. The residue smoulders away in contact with the air, leaving a black powder (probably platinum and oxide of copper). This powder, when boiled with nitric acid, furnishes copper to the acid, and spongy platinum remains behind; but from several experiments the author is convinced that all the copper cannot be extracted in this way. Repeated evaporation of nitric acid over the powder and calcination of the residue, as done by Quadrat, certainly destroys every trace of protocyanide (or paracyanide); but it renders the calcined sponge so compact, that it cannot be separated from the crucible, nor does it give off all its copper to boiling acids. The author found it best to lay the finely powdered and weighed substance in as thin a stratum as possible upon a flat platinum dish, and to let it burn first of all at a gentle heat; then to calcine it strongly for a considerable time in a muffle, and finally to fuse it with bisulphate of potash. When suspended in water and treated with chlorine gas, the compound is very slowly attacked; shining green crystals are produced, which the author will describe in his second memoir as pereyanide of platinum and copper. When boiled with hydrated sulphuric acid for half an hour, the salt remains quite unaltered; this is also the case with sulphuric and nitric acids. The author however remarks particularly, that he employed in the formation of his copper-salt a protocyanide of platinum and potassium, prepared according to Quadrat's (or rather Knop's first) method, which had only been once recrystallized, and therefore was represented by the formula PtCy^2K^6 . Analysis gave:—

	Calculated, CuPtCy ² .		Found.		Calculated according to Quadrat, Cu ⁶ Pt ⁵ Cy ¹¹ .	
Pt	99	= 54.10	(55.98)	54.09	495	= 50.87
Cy	52	28.41	..	..	286	29.40
Cu	32	17.49	..	..	192	19.73

Protocyanide of Platinum and Mercury.—A solution of protocyanide of platinum and potassium furnishes a white precipitate with bichloride of mercury. With protonitrate of mercury it gives a precipitate, which is at first white, but as the quantity of the reagent is increased becomes yellow, then green, and at last of a fine blue; whilst in the fluid the colour is deep, but when it is filtered and dried it becomes of a cobalt-blue, which is rendered paler by hot water until it becomes gray. Döbereiner had previously noticed these facts, and explained them correctly by stating the white compound to be protocyanide of platinum and mercury, the blue to be the same + protonitrate of mercury, which latter may be extracted by hot water. Rammelsberg's analysis has since completely confirmed Döbereiner's view with regard to the blue salt, as he found it to be composed according to the formula $5\text{PtCy}^2\text{Hg} + \text{Hg}^2\text{O}, \text{NO}^5 + 10\text{HO}$. The white salt which Döbereiner employed in the preparation of the protocyanide of platinum has not yet been analysed, as Quadrat found that both the white and the blue salts were decomposed in drying, globules of mercury being sublimed on the walls of the drying apparatus. The author found that the blue salt obtained with protonitrate of mercury cannot be entirely freed from the nitrate by washing with water, even when the wash-water is no longer rendered brown by sulphuretted hydrogen. The salt always remains of a bluish-gray, which becomes particularly apparent on drying. If the salt be washed as much as possible, powdered, placed in a thin layer upon a flat dish covered with a glass plate, and exposed to a temperature of 392° to 482° F. (in the sand- or air-bath), it gradually becomes snow-white, and the glass plate is covered with small globules of mercury. If these be rubbed off when the salt has become quite white, it may then be heated for any time to the same temperature without giving off any more mercury. Above 572° F. the salt becomes slightly brown, but without changing its composition, as the author found from analysis. If the salt, thus prepared and completely dried, be then put into a platinum crucible, covered with a watch-glass, and slowly heated to redness, the glass is seen to be coated with mercurial vapours, which however soon disappear, whilst cyanogen is evolved, and may be recognized by its odour and flame. By this process the white salt is converted into yellow protocyanide of platinum, which remains unchanged for some minutes in the crucible at a moderate red heat, and only becomes converted, with loss of cyanogen, into a black mass at a bright red heat; this mass quickly burns into spongy platinum when exposed to the air.

Quadrat did not analyse the salt, but deduces its composition in the following manner:—As the potash-salt, $\text{K}^6\text{Pt}^5\text{Cy}^{11} = 5\text{KPtCy}^2 + \text{KC}_y$, the fluid, after the precipitation with an excess of proto-

nitrate of mercury, must always contain cyanide of mercury, if the precipitate were HgPtCy^2 instead of $\text{Hg}^6 \text{Pt}^3 \text{Cy}^{11}$; but he could find no cyanide of mercury. The author prepared his salt from his potassium compound. It was white, but a second preparation had a pale brownish tinge. Analysis gave:—

	[Calculated, HgPtCy^2 .]	Found.			Calculated, $\text{Hg}^6 \text{Pt}^3 \text{Cy}^{11}$.
Pt	99=39.44	38.36	39.72	39.55	495=35.68
Cy^2	52 20.72	..	..	..	285 20.71
Hg	100 39.84	..	..	..	600 43.45

Protocyanide of Platinum.—This body was first prepared by Döbereiner, by the very gentle calcination of protocyanide of platinum and mercury in closed vessels; it formed a yellowish-green powder, which was extremely indifferent to reagents. Knop and Schnedermann showed that it could also be obtained by heating anhydrous protocyanide of platinum and potassium with perchloride of mercury, a process which, in the main, coincides with that of Döbereiner; but a second mode of preparation, discovered by them, is of more importance. Protocyanide of platinum, prepared in the dry way, is perfectly insoluble in reagents, especially in solutions of protocyanides; it is consequently of no use in the preparation of double cyanides. But if protocyanide of platinum and potassium or ammonium be boiled for a long time with sulphuric acid, a gelatinous body, of a fiery orange-yellow colour, is separated; this is quite insoluble in the fluid in which it is formed, and settles well from it; but in pure water it diffuses itself to such an extent, that the mixture appears like a solution, and is extremely difficult to filter. It is readily soluble in percyanide of potassium, ammonium, &c., and thus affords a means of preparing very pure salts. It is only changed by boiling for a long time with sulphuric acid; sulphurous acid is evolved, and the colour becomes olive-green. It always obstinately retains a little potash-salt, which cannot be extracted in any way. When dried, it shrinks together to an incredible extent, and forms shining, reddish-brown, fissured masses, like aloes or shell-lac, consisting of an orange-brown powder.

Döbereiner found 78 to 79 per cent. of platinum in his preparation, and Knop a little more than 76 per cent. in his. Quadrat analysed both products, and found in both only 71.7 and 72.8 per cent. of platinum, which agrees most nearly with $\text{Pt}^2 \text{Cy}^3$, from which it would follow that this body is a sesquicyanide, and that the protocyanide has not yet been prepared; but the circumstance, that when dissolved in cyanide of potassium it again furnishes protocyanide of platinum and potassium, is against this.

The author has repeatedly prepared Knop's product, and at the same time has also adopted another method, namely, continued exposure of pure protocyanide of platinum and ammonium to a heat of 572°F . on the sand-bath. The yellow crystals first become pure white (anhydrous), and then they begin to acquire a yellow

colour, at the same time evolving a light and very penetrating vapour (cyanide of ammonium). At last there remain beautiful sulphur-yellow pseudomorphous crystals of protocyanide of platinum, which, when more strongly heated, smoulder away on the access of air, leaving spongy platinum in distinct pseudomorphous crystals. When platinocyanic acid is boiled with nitric acid, a very pure protocyanide of platinum is produced, together with other products, which however the author leaves for his next memoir. Analysis:—

Calculated,		Found.				
Pt ² Cy ³ .	Pt ⁹ Cy ¹¹ .					
198=71·94	891=75·70	75·24	75·59	76·05	76·36	77·18
78 28·26	286 24·30					
Calculated.						
Pt ¹⁰ Cy ¹¹ .		PtCy.				
990=77·59		99=79·20				
286 22·41		26 20·80				

These numbers evidently confirm Knop's result (76 to 77 per cent. of platinum). If a formula were adopted for every analysis, we should have to admit a dozen protocyanides of platinum; all the above products are evidently protocyanide with 79·20 per cent. of platinum, but contaminated with variable quantities of matters, which cannot be got rid of by washing.—*Sitzungsber. der Akad. der Wiss. zu Wien*, xvii. p. 57.

Note on the Double Salts formed by the Chlorides of Cadmium, Bismuth, and Uranium with the Organic Alkaloids. By C. GREVILLE WILLIAMS, Assistant to Dr. Anderson, Glasgow University*.

Croft, and, more recently, Von Hauer†, have shown that the chlorides of ammonium, the fixed alkalies, and the alkaline earths form well-crystallized double salts with chloride of cadmium. Before seeing the results of the latter chemist, I had ascertained that the organic alkaloids formed double salts with chloride of cadmium. In fact, the differences in the behaviour of bases with this substance may, in some researches, be made available as a means of discrimination.

When tolerably concentrated solutions of hydrochlorate of choline and chloride of cadmium are mixed, the whole solidifies into a hard mass of crystals, which, when washed with alcohol and dried at 212°, gave on analysis, the carbon, hydrogen, chlorine and cadmium being estimated, numbers exactly agreeing with the formula C¹⁸ H⁷ N, HCl, + 2CdCl, corresponding in constitution therefore with the chlorobiscadmates of M. von Hauer.

* Communicated by the Author.

† Chem. Gaz., Nov. 15, 1855.

Aniline immediately yields crystals under the same circumstances, but does not solidify unless the solutions are extremely concentrated.

Chloride of cadmium added to hydrochlorate of lepidine, causes the formation of crystals after a short time.

The corresponding salts of nicotine and cinchonine are obtained with greater difficulty.

When rather strong solutions of chloride of bismuth and hydrochlorate of chinoline are mixed, the fluid solidifies into a mass so hard as scarcely to yield to the pressure of a glass rod applied with moderate force; the compound formed is almost insoluble in water, but dissolves readily in hot hydrochloric acid, and is deposited on cooling in silky needles.

Uranium also forms a double salt of great beauty with hydrochlorate of chinoline; it appears to be analogous in constitution with the hydrochlorate of uranic oxide and ammonia.

The double salts of the chlorides of several bases and metals are under study.

The details of the experiments belong to investigations which have been in progress for some months, the above slight outline being given in consequence of the publication of M. von Hauer's last paper.

On Colombian Guano, and certain Peculiarities in the Chemical Behaviour of Bone-phosphate of Lime. By CAMPBELL MORFIT, M.D.*

This guano was originally introduced into commerce as "*Maraicao guano*," and hence it is supposed to come from some islands in the Carribean Sea near the coast of that country. Its source, however, is not definitely known, except to those who monopolize the trade in the article.

Its high character as a fertilizing agent, and the discordant results of analyses already on record, having prompted a careful examination of it, I herewith present a report of my research.

As brought, it is in lumps, with a compact interior of a chocolate-brown colour, and a grayish-white mammillated exterior resembling an enamel. Between this enamel-looking portion and the compact interior is a lighter brown porous structure. The whole reduces without much difficulty under the pestle with a dull even fracture, and gives a brownish-gray powder.

To ensure the complete integrity of the investigation, a large sample of several pounds was procured directly from the State Inspector, and a fair average adjusted by selecting in equitable proportions about 4 oz. from the different phases of the whole mass. The natural form is preferable for analysis, because the powdered article of commerce is liable to admixture with foreign matters, which get in, accidentally or otherwise, during the process of grinding.

* Communicated by the Author.

The numbers obtained from it are as follows:—

Accidental moisture	0.500
Constitutional water, expelled at 212° F.	1.500
Constitutional water, expelled above 212° F.	5.100
Organic matter soluble in acid	1.490
Organic matter soluble in water	0.800
Organic matter insoluble in either acid or water.	0.340
Sand and insoluble inorganic matter	0.490
Carbonic acid	0.060
Chloride of ammonium	0.090
Soda	traces
Magnesia (soluble)	0.010
Phosphate of lime (soluble).	0.210
Sulphuric acid	3.230
Phosphate of iron ($\text{Fe}^2 \text{O}^3$)	0.920
Phosphoric acid	39.587
Lime	40.565
Phosphate of magnesia.	5.930
	100.822

Specific gravity 2.28

The accidental water was estimated by drying a given quantity of fine powder *in vacuo* over sulphuric acid, and noting the loss of weight. This latter, deducted from the further loss sustained by heating the residue over a water-bath until the weight became constant, gave that part of the constitutional water expelled at 212° F.

The remaining water of constitution was determined by heating a new quantity of the guano in an atmosphere of carbonic acid, taking the weight of the aqueous distillate, which is the totality of water in the guano, and deducting from it the preceding two weights.

To ascertain the gross amount of volatile matter, a given portion was incinerated, and the calx weighed for loss. When at a subsequent stage the carbonic acid, chloride of ammonium, and organic matters soluble in water and acid, were severally determined, being a part of the gross volatile matter, they were, together with the combined weight of the three waters, subtracted from it to get the weight of organic matter soluble in acid, as expressed by the residue.

A separate quantity of 200 grs. was taken for the soluble matters, and digested with 16 fluid ounces of distilled water in successive instalments, filtered and washed. The filter was discarded, and the filtrate evaporated over the water-bath to one-fifth of its volume, after which it was divided by weight into two equal portions, A and B.

From A the sulphate of lime was precipitated by alcohol, and after twelve hours' repose filtered off and washed with dilute alcohol. Not deeming it expedient to estimate the sulphate of lime in this way, owing to the uncertainty of dissolving out the entire content even with a large volume of water, the filter was discarded. The filtrate, after evaporation over the water-bath to drive off alcohol,

was treated with ammonia, which threw down the phosphate of lime existing as biphosphate. This being separated by rapid filtration, the filtrate was set aside for twenty-four hours, at the end of which time crystals of NH^3 , HO , 3MgO , PO^5 , 12HO , had formed from the magnesia combined with the phosphoric acid which was (as will hereafter be shown) retained in the liquid, the normal state of the magnesia having been sulphate.

The soluble organic matter was estimated from B by adding a slight excess of caustic soda-ley to promote elimination of the ammonia, and carefully evaporating to dryness in a counterpoised platina crucible over a sand-bath, and noting the weight when it became constant; the organic matter having been then burned off over the naked fire, the weight was again taken, so as to get the loss which represents its amount.

To separate the ammoniacal salt, which in preliminary qualitative examination was found to be the chloride, but in very minute proportion, I employed a method which yielded only approximate results, but sufficiently exact under existing circumstances.

To avoid any possible loss by volatilization in the use of hot water, a fresh quantity of 100 grs. of powdered guano was displaced with cold water, and the solution evaporated over the water-bath as before, but in this instance the soda-ley being omitted. When the weight became constant it was noted, and a red heat afterwards applied, and continued until the entire expulsion of both the ammoniacal salt and organic matter. As the loss of weight by this last heating represents these two latter combined, it was only necessary to subtract from it the weight of organic matter previously determined in B, to ascertain that of the chloride of ammonium. For the sulphuric acid and insoluble matters, another 100 grs. of the powdered average was digested in pure nitric acid at 212°F ., to perfect solution; that which is of uncertain attainment when hydrochloric acid is used, as it acts slowly, and in some instances imperfectly, and may possibly leave some of the guano undissolved. The solution was diluted and filtered upon a weighed filter, washed with hot water, dried over the water-bath and *in vacuo* to get its constant weight, then incinerated, and the calx weighed as sand and insoluble inorganic matters. This latter, deducted from the constant weight of the unburned filter, gave the amount of organic matter insoluble in either acid or water.

The sulphuric acid was separated from the filtrate with nitrate of baryta, and deduced by calculation from the precipitated sulphate of baryta, which was well washed with nitric acid and hot water previously to being ignited.

Although the filtrate from the sulphate of baryta might be used for the estimation of the remaining components, lime, magnesia, iron and phosphoric acid, we deemed it advisable to reject it, as the precipitate from so large a quantity of guano as 100 grs. might be bulky and not nicely manageable. A new portion of 20 grs. was therefore substituted, and digested in nitric acid, and filtered as before. The lime was then precipitated from the filtrate by pure

sulphuric acid and alcohol, and filtered off after several hours' repose, washed with dilute alcohol, ignited and weighed, and the lime deduced by calculation from the sulphate. The entire absence of lime from the filtrate having been proved by testing a drop with oxalate of ammonia, it was then evaporated over the water-bath to drive off alcohol, superneutralized with aqua ammoniæ, left at rest twenty-four hours for the subsidence jointly of the phosphate of magnesia and phosphate of iron, and filtered. The filtrate having been set aside, covered, and marked as C, the filter was displaced with hot acetic acid, which dissolved out the magnesia-salt and left the phosphate of iron. This latter was then washed, dried and ignited. Ammonia was in the meantime added to the filtrate, which after some hours dropped all the phosphate of magnesia retained in solution by the acetic acid.

From the filtrate C all the remaining phosphoric acid was separated by a clear solution of sulphate of magnesia, and filtration after twenty-four hours' repose.

The carbonic acid was determined in the usual way, by means of Bunsen's apparatus.

Upon critical examination of the results, it will be observed that the lime, magnesia, phosphoric acid and water are in such proportions that it is impossible to combine them together in accordance with any known formulæ. After minor allotments of lime to the sulphuric and carbonic acids, and the apportionment of the phosphoric acid due to the phosphate of lime to restore it to its original state of biphosphate, there is, with that portion to be taken from the phosphate of iron (naturally existing as Fe^2O^3), enough phosphoric acid to convert all the residual lime into bone or tribasic phosphate (3CaO PO^5), and 7.171 grs. to spare. Now the figures do not allow the hypothesis, that a part of the phosphate of lime may be neutral phosphate. Nor can any of the lime and phosphoric acid be combined as biphosphate in allotropic condition; for though it is true that biphosphate of lime loses its solubility upon being highly heated, yet the physical characters of the guano, and the presence of water and organic matter, preclude the possibility of its having undergone igneous action. Moreover, it was found that cold water, even in large quantities, would not dissolve out a greater quantity of phosphate than 0.210. Still it must be mentioned, that, on the other hand, certain peculiarities of behaviour were encountered in preliminary essays. It was observed that the filtrate from the precipitate thrown down in a nitric solution of guano at 212°F . by aqua ammoniæ invariably retained phosphoric acid, and in one instance estimated to the amount of 4.27 per cent. When the precipitation was in the cold, there was always an accompaniment of lime; but when the nitric solution was boiling, and the precautions recently directed by Denham Smith* were strictly observed, the proportion of lime was reduced to mere traces. On repeating these experiments with pure bone-phosphate, and also with bone-black,

* Chem. Gaz., 1855, p. 203.

precisely the same results ensued. What relation to quantity may exist between the circumstance of temperature, state of dilution and acidity, is a matter for future experiment and explication. Suffice it to say, that phosphoric acid was always left in solution with the ammonia; and what is also remarkable, the phosphate of lime thrown down from the *hot* nitric solution of guano always presented, to a limited extent, a most obstinate resistance to the solvent action of acetic acid; thus indicating the formation, under the circumstances, of an unknown compound, or the assumption of a passive state.

The question then arising as to the original condition of the phosphoric acid retained by the ammonia, an experiment was instituted to determine whether it could possibly have been uncombined. 100 grs. of the guano were boiled in successive portions of distilled water, and the mixed liquids filtered. The filtrate gave an instantaneous acid reaction, and, upon being treated with ammonia and left to repose, dropped both the phosphates of lime and magnesia, there being not even a trace of lime-salt left in solution. When these were filtered off, and the filtrate treated with sulphate of magnesia and chloride of ammonium, it yielded upon repose 2.11 grs. phosphate of magnesia = 1.35 gr. phosphoric acid. This result having recalled the fact of neutral phosphate of magnesia being easily decomposed by continual boiling with water into free phosphoric acid and a basic phosphate ($3\text{MgO}, \text{PO}^5 + 7\text{HO}$), the portion of phosphoric acid in question was about to be referred to that source, when, as a suggestive of the over-large quantity and of the above-noted peculiarity of magnesian phosphate, the experiments were extended to comprise pure bone-phosphate of lime, and with nearly analogous results. When boiled with hot water and filtered, the filtrate gave an immediate precipitate of phosphate of lime with ammonia. The same filtrate, after being entirely freed of lime by pure sulphuric acid and alcohol, gave, when treated with a mixture of chloride of ammonium and sulphate of magnesia, a considerable quantity of ammonio-magnesian phosphate. A decomposition of the bone-phosphate by the boiling water was thus evident, but in a different degree from the phosphate of magnesia; for the phosphate of lime, in leaving a portion of its acid free, separates partly in a soluble form, whereas the basic magnesian salt formed under the same circumstances is insoluble.

These facts having indicated the inadmissibility of hot water for the experiment, 100 grs. of the average sample of guano were then treated with cold water in a displacement-tube of 1 inch diameter and 2 feet length. The clear liquid running through contained some little biphosphate of lime, but only traces of free phosphoric acid.

In conclusion, therefore, it follows from these experiments,—

1. That Colombian guano does not contain either free phosphoric acid or soluble phosphates, in proportion beyond the 0.329 of biphosphate of lime.

2. That, as Denham Smith had previously shown*, there are

* Chem. Gaz., 1855.

certain precautions requisite, as regards temperature and state of dilution, to ensure the entire precipitation of lime by ammonia from an acid solution of bone-phosphate.

3. That in precipitating phosphates of lime and magnesia with ammonia from an acid solution, under the ordinary circumstances as well as those above mentioned, there is always a variable portion of phosphoric acid left in solution; and therefore this method, so generally followed for the quantitative estimation of the earthy phosphates in guano, is inaccurate.

4. That bone-phosphate of lime is partially decomposed by prolonged boiling with hot water into free phosphoric acid and a soluble phosphate of lime.

5. That the atomic constitution of the earthy phosphates is still an open question, and consequently correct formulæ cannot be constructed from my results.

6. That Colombian guano is rich in phosphoric acid and lime; and theoretically, as to those constituents, its money-value is far greater than that of bones.

University of Maryland, Baltimore,
October 1, 1855.

On the Composition of Fulminating Mercury and Isocyanuric Acid.
By L. SCHISCHKOFF.

[Concluded from page 425.]

A slightly heated solution of nitrate of mercury, acidulated with nitric acid, dissolves a large quantity of fulminating mercury; when further heated, a violent evolution of carbonic acid and nitrogen is produced. At the same time a yellow precipitate is formed; this is blackened by ammonia, and when the mercury is separated from it by sulphuretted hydrogen, a mixture of two acids is obtained. The fluid from which the yellow precipitate is produced contains a large quantity of protonitrate of mercury when the operation is complete.

To separate the two acids thus obtained, the author saturated them with ammonia, evaporated the fluid to dryness, and treated the mass with absolute alcohol. The portion left undissolved, when recrystallized from water, produced a precipitate containing nitrogen with salts of lime and baryta, and an extremely explosive salt with salts of silver. That which dissolved in the alcohol did not precipitate lime-salts; with nitrate of silver it produced a detonating salt, which also contained nitrogen.

As far as could be judged from their outward appearance, the acids produced by the action of nitrate of mercury upon fulminating mercury, are the same as those obtained by the action of nitrous acid and of muriatic acid and the alkalies upon isocyanuric acid. The pernitrate of mercury, during its conversion into the protosalt, exerts the same action upon the fulminating mercury that would be produced by nitrous acid; only in this case the action takes place better and more readily, because the fulminating mercury is in solution.

The yellow precipitate obtained by the action of chloride of

potassium upon fulminating mercury, contains the elements C, NCl, HgO, and H; but its analysis did not lead to an exact formula.

A solution of caustic potash, even when very concentrated, has no action upon fulminating mercury at ordinary temperatures; but when the solution of potash is heated, and fulminating mercury is then added to it in small portions, a very violent reaction is produced at each addition; the fluid becomes heated to such a degree that it boils strongly, and an olive-green precipitate is formed. Cyanate of potash remains in the fluid. While this reaction is going on, no evolution of ammonia takes place; but when the operation is concluded, and the excess of potash is saturated with an acid, the fluid contains a large quantity of an ammoniacal salt. A portion of the nitrogen is contained in the precipitate, for when this is dissolved in muriatic acid, besides protochloride of mercury, the salt $2\text{ClHg} + \text{ClNH}^4 + \text{HO}$ is produced, and crystallizes on evaporation.

The olive-green precipitate was formerly regarded as protoxide of mercury, and on this account alone some chemists regarded fulminating mercury as a protosalt. The solubility of fulminating mercury in muriatic acid, and the comparison of its elementary composition with that of fulminating silver, show distinctly that this is not the case.

The author is of opinion that fulminic acid in its nature approaches much more closely to the amides than to the acids, and that the metals in the fulminates are not in the condition of salts, but displace the hydrogen in the ammonia in the same way as in Plantamour's compound, NHg^3 .

The crystalline forms of the potash- and ammonia-salts of isocyanuric acid, as determined by A. Gadolin, belong to the monoclinohedral system. The two salts are isomorphous, as may be seen from the following measurements. The clinodiagonal being taken as unity, the following values were calculated:—

	Potash-salt.	Ammonia-salt.
For the principal axis	1·2314	1·2925
For the orthodiagonal	0·5336	0·5357
For the inclination of the principal axis to the clinodiagonal	83° 18'	81° 4'

Bull. de St. Pétersb., Classe Phys. Math., xiv. p. 98.

Note on the Production and Preparation of a new Green Colouring Matter. By M. VERDEIL.

I have succeeded in extracting from the artichoke, and several other plants belonging to the family of the *Compositæ*, a green colouring matter, which is very distinct from chlorophyll, and possesses peculiar characters, which appear to assimilate it to the Chinese green of which M. Persoz has given a description to the Academy of Sciences*. The process which I employ for the production of this colouring matter consists in the simultaneous action

* See Chem. Gaz., x. p. 458.

of air, ammonia, and water upon the bruised artichoke plant, or on certain parts of the plant, especially the flowers. This action appears to be identical with that exerted by the same agents upon the formation of orchil. The resemblance is indeed so great, that I have succeeded in isolating from the flowers of the artichoke, principally from the base of the petals, a white fecula, which separates easily as a deposit. This fecula contains the greater part of the colouring principle of the artichoke. It is this mixed with water that I expose to the simultaneous action of ammonia and the oxygen of the air, by constantly agitating the liquid. Extracts obtained by hot water from the heads of the artichoke also furnish a magnificent green colour. I have already obtained results which lead me to believe that this colouring matter may be used in dyeing and printing stuffs.

As soon as the colour is completely formed, the alkaline liquid may be precipitated with acetic acid. A voluminous green precipitate is formed, and may be filtered upon linen. This precipitate is soluble in solution of ammonia or carbonate of soda. It is of a very fine green. When washed with hot water, pressed and dried, it has the appearance of cakes of indigo; but it is of a green colour, and furnishes green solutions.

I have also obtained lakes, but have not yet studied them sufficiently.—*Comptes Rendus*, October 15, 1855, p. 588.

On a Process for coating Copper and Brass with Platinum by the Electrottype. By M. JEWREINOFF.

By means of a moderately strong battery these two metals may be coated with platinum. The objects must be removed from the bath from time to time, and polished with whiting, and then again exposed to the current. The bath consists of a solution of prot-oxalate of platinum.—*Polytechn. Centralbl.*, 1855, p. 1210.

ANALYTICAL CHEMISTRY.

A new Process for the Analysis of Chrome-Ores.
By PETER HART*.

IN almost all the methods recommended for the analysis of this mineral, the principle has been to mix it at once with a highly-oxidizing flux, to convert the oxide of chromium into chromic acid. Many ingenious processes have been devised to facilitate the operation, amongst others that of mixing it with some non-active substance to keep the mixture in a porous state to favour the oxidation (Calvert); it has also been proposed to remove some of the other bodies present in the ore before submitting it to the oxidizing process (Rivot). Hunt fuses the mineral with an alkaline bisulphate,

* Communicated by the Author.

producing a salt of chromium, which he decomposes by an alkaline carbonate, again producing oxide of chromium in a state of division impossible to be obtained by any amount of pulverization; the oxide of chromium thus obtained is capable of being oxidized with the greatest ease into chromic acid. My process is based on the same principle as the one last described, and combines its ease and accuracy without its disadvantage of filtering, washing and drying the precipitated oxide, as though the same operations of solution and oxidation are gone through consecutively, yet they are done in one operation. The following is the process:—About 20 grs. of the pulverized ore is projected into seven or eight times its weight of fused baborate of soda (borax) contained in a platinum crucible; it is stirred up, and thoroughly mixed together by means of a stout platinum wire or slip; the cover (which has a bit cut out to allow the slip to remain in during the fusion) is now put on, and the crucible maintained at a white-red heat for half an hour. (For this purpose I find my gas-furnace, described in page 175 of this volume, admirably adapted.) At the end of this time, during which it must have been occasionally stirred, dry carbonate of soda in fine powder must be added until effervescence ceases, that is until the baborate has become converted into neutral borate of soda. Now project by small quantities at once about three times the weight of the ore employed, of a mixture of equal parts of nitre and carbonate of soda; at this point almost constant stirring is necessary to prevent the mass frothing over; after this about five minutes' fusion is all the time necessary to complete the oxidation, by conversion of the sesquioxide of chromium, Cr^2O^3 , into chromic acid, CrO^3 , which is obtained of course as chromate of potash. It now lies at the option of the operator whether he boils the crucible and spatula in hydrochloric acid, thus obtaining the whole of the constituents of the ore in solution, from which they can be individually separated by any of the ordinary processes; or adopts the plan which I prefer (that is, if the amount of oxide of chromium is all that is required to be known), of digesting the crucible in hot water until all the soluble salts are removed, filtering, and estimating the chromate in the filtrate, by what is known as Dr. Penny's process, viz. by protochloride of tin. In order to see if the operation has been successful, the insoluble portion remaining on the filter may be digested in hydrochloric acid, when any unacted-upon particles of ore will be left undissolved; but if the above instructions have been adhered to, and the ore finely powdered, none will be found.

The following is an example:—An acid and dilute solution of protochloride of tin was prepared while the fusion was going on. When finished, the chromate obtained was put into a capacious flask, and rendered acid by hydrochloric acid; the test-solution of protochloride was then added until the yellow colour had almost disappeared. A little iodide of potassium and starch-water was then added; the contents, of course, instantly became intensely blue. The test-solution was then added carefully drop by drop until the blue colour suddenly disappeared. The number of measures em-

played were then noted. The following are the notes:—15 grs. ore employed took 87 measures of SnCl solution (164 of which represent 20 grs. bichromate); consequently the 15 grs. ore represent $10\cdot6$ bichromate $= 5\cdot6 \text{ Cr}^2 \text{ O}^3$; or in 100 parts $37\cdot3 \text{ Cr}^2 \text{ O}^3$ or $70\cdot6$ bichromate of potash.

On the Approximate Estimation of Prussiate of Potash.

By J. W. SLATER, Esq.*

It is known that when a solution of the permanganate of potash is dropped into ferrocyanide of potassium, the yellow prussiate of commerce, it undergoes instantaneous reduction. The crimson of the permanganate changes to a bright green, which in turn passes to a chestnut-brown, and hydrate of peroxide is finally deposited.

Upon this reaction may be founded a simple and expeditious method of ascertaining the value of a sample of prussiate. The ordinary impurity, sulphate of potash, may be detected, and its amount determined by a salt of baryta. But this process, though simple to the chemist, presents difficulties to the manufacturer, and even in skilful hands extends over a considerable amount of time.

As alkaline sulphates (and chlorides if present) exert no reductive action upon the red permanganate, it follows that the amount of this salt decolorized must be proportional to the amount of true ferrocyanide present.

A known weight of pure prussiate is dissolved in water, considerably diluted, and preserved as a standard. A solution of the permanganate, obtained from the crystalline salt, is also requisite. This latter, if preserved in well-stoppered bottles, undergoes little change; still, at each operation, its exact strength should be ascertained by means of the standard solution. The solution of prussiate is placed in a wide, shallow, porcelain vessel over a small lamp, and the permanganate added from an ordinary graduated pourette. When the drops, on falling into the prussiate, no longer turn a bright emerald, but a sea-green, the whole must be frequently stirred, and further additions made with great care. When a green shade no longer appears, the operation is complete; and by comparing the number of degrees of permanganate employed with the amount required for a pure specimen, the per-centage of alkaline sulphates will at once appear. The residual liquid is ferridecyanide of potassium, mixed with carbonate and hydrate of potash, and has a decidedly basic reaction.

As the permanganate is without action upon the red prussiate, it may very conveniently serve as a test for regulating the manufacture of the latter. As long as a drop when added turns green, undecomposed yellow prussiate is present.

Sheffield Mechanics' Institution,
October 26, 1855.

* Communicated by the Author.

THE CHEMICAL GAZETTE.

No. CCCXVI.—December 15, 1855.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Products of Decomposition of Nitrobenzole and Nitrotoluole by Sulphite of Ammonia. By L. HLIENKAMP.

THE material employed in this investigation consisted of the so-called commercial benzole, that is to say, rectified light coal-tar oil. The author purified it by treatment with sulphuric acid and potash, and decomposed it by fractional distillation into oils of different boiling-points. The fractions with a boiling-point of 144° to 153° F. served for the preparation of nitrobenzole; those boiling at 230° to $234^{\circ} \cdot 5$ F. furnished the nitrotoluole; and those with a boiling-point of 293° to 302° F. were employed in the preparation of nitrocumole.

The nitro-compounds prepared by treatment with nitric acid were treated with sulphite and carbonate of ammonia. The latter is necessary, because with sulphite of ammonia alone the derivative produced is again decomposed, as the fluid becomes acid.

The *nitrobenzole* appeared from the results to be a mixture of nitrobenzole and binitrobenzole. 80 grms. of it were distilled with 340 grms. of dry sulphite of ammonia, a litre of absolute alcohol, and a little solid carbonate of ammonia. After boiling for eight or ten hours, the reduction was complete. This point is known to be attained when a sample of the fluid is no longer rendered turbid by water.

The fluid is allowed to cool. After standing one or two days, all the sulphite of ammonia separates from the alcohol. It is then filtered, and the filtrate, which has a neutral reaction, is evaporated slowly to an oily consistence. During this also the fluid must be kept alkaline by the addition of some carbonate of ammonia. The brownish-red oily fluid thus obtained, when left for forty-eight hours, deposits crystals of two kinds; the largest quantity by far consists of fine soft laminæ; the rest are slender hard needles. The author only succeeded in obtaining the product which crystallizes in needles. As it is the ammoniacal salt of an acid which appears to have originated from binitrobenzole, the author calls it

Bithiobenzolic Acid.—It has the formula $C^{12} H^8 N^2 S^4 O^{12}$. It is produced in this case in the same way as the thionaphthionic and thionaphthamic acids in the experiments of Piria, who first indicated the use of sulphite of ammonia in the reduction of organic bodies. Thus $C^{20} H^7 NO^4 + 6(NH^4 O, SO^2) = C^{20} H^{12} N^2 S^2 O^6 + 4(NH^4 O,$
Chem. Gaz. 1855.

SO^3) + NH^3 (Piria). In this case also the ammoniacal salt of bithiobenzolic acid = $\text{C}^{12} \text{H}^{14} \text{N}^4 \text{S}^4 \text{O}^{12}$ or $\text{C}^{12} \text{H}^8 \text{N}^3 \text{S}^4 \text{O}^{12} + 2(\text{NH}^3)$ is produced in accordance with the equation: — $\text{C}^{12} \text{H}^4 \text{N}^2 \text{O}^2 + 12(\text{NH}^4 \text{O}, \text{SO}^2) = \text{C}^{12} \text{H}^{14} \text{N}^4 \text{S}^4 \text{O}^{12} + 8(\text{NH}^4 \text{O}, \text{SO}^3) + 2\text{NH}^3$; and it is probable that the second body mentioned above as crystallizing in laminæ, was the similarly produced body $\text{C}^{12} \text{H}^{10} \text{N}^2 \text{S}^2 \text{O}^6$, representing nitrobenzole.

Bithiobenzolate of Ammonia, $\text{C}^{12} \text{H}^8 \text{N}^3 \text{S}^4 \text{O}^{12} + 2\text{NH}^3$, crystallizes in needles, and is in the highest degree soluble in water and aqueous alcohol. It dissolves with great difficulty in absolute alcohol, and is insoluble in æther. When heated on platinum foil, it puffs up and carbonizes without previous fusion. During this the odour of sulphurous acid is perceptible. The aqueous solution has a slightly acid reaction, but it gives no reactions worthy of notice with the salts of other acids. Nitrate of silver alone furnishes a precipitate of metallic silver after standing some time. The solutions of many salts, on ebullition, give important reactions. Perchloride of mercury gives a precipitate of protochloride; perchloride of iron renders the solution opalescent, and when the boiling is continued a yellow precipitate is deposited; ferrocyanide of potassium renders the solution turbid, and a slight odour of hydrocyanic acid is perceptible; ferridecyanide of potassium acts in the same manner, but the opalization is produced with more difficulty. The blue solutions of sulphate and perchloride of copper are rendered green by the aqueous solution of bithiobenzolate of ammonia, even in the cold. When heated, the former becomes turbid and opalescent; the latter becomes intensely dark green when boiled, but remains clear. Muriatic and sulphuric acids, even when concentrated, have no action in the cold; when heated, a peculiar sweet odour is perceptible, together with the evolution of a pungent gas. The vapours given off did not show the reaction of sulphurous acid with chromate of potash. Nitric acid gives an orange-yellow colour to the solution even in the cold, but especially when heated; in other respects it behaves like muriatic and sulphuric acids. Chlorine produces traces of a brown resinous body, with a large quantity of chloranile, which swims upon the fluid in its characteristic yellow laminæ. The analysis of the salt gave,—

C	24.63	24.45	12	23.84
H	4.82	4.94	14	4.64
N	18.20	18.20	4	18.54
S	21.25	21.17	4	21.19
O	31.10	31.24	12	31.79

Bithiobenzolate of Baryta, $\text{C}^{12} \frac{\text{H}^6}{\text{Ba}^2} \text{N}^2 \text{S}^4 \text{O}^{12}$, is obtained by putting the ammoniacal salt into boiling baryta water, and boiling it until the ammonia is volatilized. The excess of baryta is got rid of by carbonic acid, and the solution is evaporated until the production of crystalline laminæ; the mother-liquor is then washed out with alcohol, as no further separation results on cooling. It is

soluble in alcohol and æther. Like the ammoniacal salt, it is anhydrous, and contains 33·73 per cent. of barium and 15·55 of sulphur (calculated, 33·97 and 15·88).

Nitrotoluole.—60 grms. of this were treated with 400 grms. of a completely saturated solution of sulphite of ammonia with the addition of carbonate of ammonia in the same manner as already described under nitrobenzole. It furnished

Thiotoluolate of Ammonia, $C^{14} \begin{smallmatrix} H^8 \\ NH^4 \end{smallmatrix} NS^2 O^6$.—It forms fine, dry, silky-white laminæ, which are soft to the touch and do not change in dry air. In moist air they acquire a red colour. When heated on platinum foil, the salt fuses into a yellow liquid before it becomes carbonized. It is insoluble in æther, but dissolves with great ease in water and watery and absolute alcohol; it crystallizes from these solutions. The aqueous solution has a slight yellowish colour, and a peculiar sweet odour; it has a slightly acid reaction. As all the salts of thiotoluolic acid are very soluble in water, no reagent produced a precipitate in this solution. Nitric, sulphuric, and muriatic acids produce no perceptible change even at a boiling heat; after long standing in the air, these acid solutions acquire a rose-colour. In course of time metallic silver is deposited from nitrate of silver, and this reaction takes place more readily in alcoholic than in aqueous solutions. Perchloride of iron gives a purple-red colour to solution of thiotoluolate of ammonia; a black precipitate is deposited on the application of heat. Perchloride of mercury, perchloride of copper, sulphate of copper, and ferro- and ferridecyanide of potassium exhibit, both in the cold and when heated, the same behaviour as with bithiobenzolate of ammonia. No chloranile is produced by the action of chlorine. This reagent separates heavy oleaginous drops of a yellow colour, which have exactly the odour of chloranile. The analysis of this salt gave,—

C	40·99	40·70	14	41·18
H	6·66	6·45	12	5·89
N	14·08	14·08	2	13·72
S	15·34	15·48	2	15·68
O	23·23	23·49	6	23·53

Thiotoluolate of Potash, $C^{14} \begin{smallmatrix} H^8 \\ K \end{smallmatrix} NS^2 O^6$, is obtained by boiling the ammoniacal salt with solution of carbonate of potash, evaporating, and extracting with boiling absolute alcohol, by which the salt is dissolved. It separates in small warts on the cooling of the solution, and forms, when dried *in vacuo*, a white crystalline powder, which has a reddish tinge. In the air it is far more stable than thiotoluolate of ammonia; it is less soluble than that salt in alcohol and water, so that it may even be obtained in crystals from the latter. The salt crystallized from its aqueous solution forms globular groups of crystals, in which the individual crystals lie close together in a radiating position around a central point. It contained 17·22 per cent. of potash (calculated, 17·41).

Thiotoluolate of Soda is obtained by means of carbonate of soda in the same way as the potash-salt; it forms small, white, wart-like crystals, which form a white powder when dried. It is readily soluble in water, but nevertheless can be obtained from it in a crystalline form; it is difficult of solution in absolute alcohol, and insoluble in æther.

Thiotoluolate of Baryta forms white crystalline crusts, which in external appearance are very like those of bithiobenzolate of baryta. It is insoluble in alcohol and æther, but dissolves readily in aqueous alcohol.

The *Lime-salt* could not be obtained in crystals.

The author has also submitted the nitro-compounds which boil between 293° and 302° F. to the same treatment. It became evident that this portion contained cumole, but it consisted principally of toluole, for by the treatment above described thiotoluolate of ammonia was again produced. It remains doubtful whether cumole furnishes a similar compound; at any rate the compound, if it exists, is not crystalline.—Liebig's *Annalen*, xcv. p. 86.

On Tartrate of Potash and Ammonia. By C. RAMMELSBERG.

The Neutral Tartrate of Potash, obtained by saturating cream of tartar with carbonate of potash, forms crystals belonging to the dimetric system, as has already been correctly stated by Hanckel. The crystals, as Rammelsberg finds, are hemihedral and hemimorphous, and they are hemihedral on the left side in proceeding from the free upper end. This salt contains 1 atom of water to 2 atoms of neutral tartrate of potash. The formula is therefore $2\text{KO}, \text{T} + \text{HO}$, in which $\text{T} = \text{C}^8 \text{H}^2 \text{O}^{10}$.

Neutral Tartrate of Ammonia, obtained from a fluid containing some free ammonia, forms crystals belonging to the monoclinometric system, like epidote. The crystals are anhydrous, and have the formula AmO, T . This requires,—

1 atom oxide of ammonium	=	325	28.26
1 atom tartaric acid	=	825	71.74

or,—

C	=	300	26.09
H	=	75	6.52
N	=	175	15.22
O	=	600	52.17

Tartrate of Potash and Ammonia is the *Tartarus ammoniacus* of the Pharmacopœias. De la Provostaye's statement, that this salt is isomorphous with the corresponding potash-salt, is correct. Its analysis gave,—

Potash		18.44	18.55
Oxide of ammonium		14.20	14.17

Dulk found this salt to contain 21.35 of potash and 12.00 of oxide of ammonium. From this the author concludes that this salt is an isomorphous mixture of the potash- and ammonia-salts, in which the

latter, which is isomorphous with the potash-salt, is contained as $2\text{AmO}, \text{T} + \text{HO}$. The samples investigated by the author contained 2 atoms of the potash-salt for 3 atoms of the ammonia-salt; that described by Dulk contained 1 atom of each.

Crystallized tartrate of potash therefore contains water, whilst tartrate of ammonia is anhydrous. Tartrate of potash and ammonia is an isomorphous mixture, with the form and composition of the potash-salt.—Poggendorff's *Annalen*, xevi. p. 18.

On the Action of Fuming Nitric and Muriatic Acids upon the Proteine Compounds. By M. MÜHLHAUSER.

The proteine compounds readily dissolve in fuming nitric acid when heated with effervescence and the evolution of nitrous fumes, but without the production of any determinate metamorphosed products. In the action of a mixture of fuming nitric acid with half its quantity of concentrated muriatic acid upon albumen, effervescence also takes place; but (if the mixture of acids has not been employed in too great excess) there remains a considerable quantity of a yellow, waxy, tough, amorphous mass, which is free from ash, insoluble in water, readily soluble in alcohol, and contains sulphur but no chlorine.

Metamorphosed products containing chlorine and hyponitrous acid, may be obtained in the following manner. One of the so-called proteine substances (such as albumen, gluten or flesh) is dissolved, with the aid of heat, in a corresponding quantity of fuming nitric acid, with the addition of water when necessary. The filtered solution, whilst still hot, is mixed in a retort with half its volume of concentrated muriatic acid, and when carefully closed submitted to a slowly increased distillation. Together with the acid vapours, there passes over a very volatile body, which violently affects the eyes, and condenses in heavy whitish drops; during the distillation the above-mentioned yellow body is formed, but gradually decomposed again, in the retort. If the distillation be then interrupted and the retort cooled, a limpid syrupous mass separates at the bottom of the retort; and of this a further quantity may be obtained by the addition of water to the supernatant fluid either immediately or after evaporation, during which it is advisable to add a little alcohol.

This non-volatile body, which may amount to 16 to 20 per cent., or more, of the dry proteine substance, forms a clear fluid, which becomes reddish or brownish when exposed to the air; it has an acid reaction, the consistence of turpentine, an unpleasant odour resembling that of oil of bitter almonds, a strong, persistent bitter taste, and a spec. grav. of 1.360. It is hygroscopic, and becomes more fluid by taking up water; when heated by itself, it fuses, becomes brown, and is decomposed without explosion, leaving a coal free from ashes; it contains no sulphur; and when treated with potash, it immediately evolves ammonia. From its analysis Mühlhäuser proposes for it the formula $\text{C}^{24} \text{H}^{12} \text{Cl}^3 \text{NO}^8$, which however was not supported by the amount of silver contained in the amor-

phous fusible silver compound prepared with it. It is separated unaltered from its solution in potash by a strong acid; it does not appear to form crystallizable compounds with bases; and its amount of chlorine is diminished by boiling it for a long time with water or nitric acid (in the latter case chlorazole is evolved, and a crystallizable compound remains).

The more volatile product of decomposition is called *chlorazole* by the author. It is a pale yellowish oil, of spec. grav. 1.555. When pure it is tolerably fluid; it has a powerful odour and a strong acid reaction; it is poisonous, and burns the skin intensely. It dissolves readily in alcohol, but very sparingly in water; it takes up no water itself, but when in contact with that fluid becomes turbid on the surface. The author expresses its composition by the formula $C^8 H^3 Cl^3 N^2 O^8$. It is decomposed by heat, and at a high temperature explodes with violence; but it may be distilled with water. The decomposition of chlorazole commences at $219^\circ F$. Hyponitrous acid is evolved, and the principal product of the decomposition is a fluid very similar to chlorazole, of spec. grav. 1.628, which passes at $284^\circ F$., and the composition of which, according to Mühlhäuser, is expressed by the formula $C^4 H^3 Cl^3 NO^4$.—Liebig's *Annalen*, xc. p. 171.

On the Atomic Constitution of Glucina. By H. ROSE.

Chemists differ in opinion with regard to the atomic constitution of glucina. It cannot be denied that it possesses stronger basic properties than any other base of the composition $2R + 3O$, and it is therefore placed by many amongst the bases $R + O$. Afdejew especially, after ascertaining the correct composition of glucina, declared himself in favour of the latter opinion.

This was however disputed first by Berzelius; and the author was also convinced, by a series of experiments, of the correctness of the constitution $2R + 3O$.

Very recently, in a paper upon glucinum and its compounds*, Debray has maintained the opinion that equal atoms of metal and oxygen are contained in glucina. The principal grounds which he adduces in favour of his view are as follows:—

Hydrate of glucina absorbs carbonic acid, and carbonate of glucina combines with the alkaline carbonates, forming crystalline double salts, which is not the case with alumina. Glucina, unlike alumina, cannot be fused with lime; for this purpose it requires the aid of alumina, silica, or some similar body, which acts the part of an acid. Chloride of glucinum cannot combine with the alkaline chlorides, in the same way as chloride of aluminium. Lastly, Debray considers that the constitution of the compounds of glucina may be expressed by simpler formulæ when the base is represented by $G + O$.

This view receives an important support from the fact, lately discovered by the author, that glucina is capable of decomposing the

* See page 386 of the present volume.

solutions of ammoniacal salts, which no other base of the composition $2R+3O$ can do. Nevertheless this fact is not, in the author's opinion, of sufficient importance to overthrow the reasons derived from his previous investigations in favour of the constitution $2G+3O$.

The author shows that alumina, when burnt in a porcelain furnace, acquires a density equal to that occurring in nature in the form of corundum, sapphire, and ruby. It has a spec. grav. of 3.99; it does not indeed exhibit a crystalline structure under the microscope, but in polarized light it gives colours, which permit one to conclude that there is a crystalline structure.

When glucina is exposed to a red heat, the loose powder exhibited a density of 3.083 to 3.09; but if it be exposed to the heat of a porcelain furnace, it is converted into a dense caked mass, which is remarkable from its possessing a density of only 3.021 to 3.027, and when examined with the microscope is found to consist of distinct, well-formed, regular prisms, exhibiting the form of corundum.

From the isomorphism of this glucina, crystallized by heating in the porcelain furnace with natural crystallized alumina, and as the latter has the same specific gravity as alumina heated in the porcelain furnace, we may well conclude that the alumina and glucina heated in the porcelain furnace are of analogous density. If the density of the latter be taken at 3.021, and that of the former at 4.0, and we suppose that both contain 2 atoms of metal and 3 of oxygen, the former will have an atomic volume of 160, and the latter of 157. These two numbers approach very closely, and from this agreement the similarity of the constitution of glucina and alumina appears evident.

But if we suppose that glucina is composed of equal atoms of metal and oxygen, its atomic volume would be 52.3. In order to compare it with the other oxides of this composition, the specific gravity of magnesia and oxide of nickel were investigated.

If magnesia be exposed to the heat of the porcelain furnace, it is obtained in a crystalline form, and exactly similar in its properties to the interesting mineral, from Vesuvius, discovered by Scacchi, and called by him *periclase*. It is apparently insoluble in acids, and is only dissolved by them after long contact. Its specific gravity is 3.694, and its atomic volume 71, consequently very different from that of glucina calcined in the porcelain furnace.

Periclase crystallizes in regular octohedra, like the crystallized oxide of nickel, which Genth separated from refined copper, and which consequently had also been exposed to a high temperature. This is also very difficult of solution in acids, and has a specific gravity of 6.605, consequently the same atomic volume as the crystallized magnesia.

We cannot therefore adopt for glucina an atomic composition similar to that of magnesia and oxide of nickel, but one like that of alumina.

The author refers to these experiments, because Ebelmen arrived at similar results by similar experiments, with this difference, that

instead of exposing the pure oxides to the heat of the porcelain furnace, he dissolved them in solvents at the same temperature, and allowed them to crystallize from these solutions on cooling, like a salt from its solution in hot water. But the numbers which he obtained agree with those of the author. He does not however refer to the author's previous memoir, although he must have been well acquainted with it, as the course of ideas followed by him in his investigations does not differ essentially from the author's. He also arrived at the same conclusions, and considered the composition of glucina to be similar to that of alumina.

The reasons adduced by Debray against this opinion may be contradicted. Like glucina, oxide of bismuth, and even alumina, peroxide of iron, and other similarly constituted oxides, can combine with carbonic acid. Like these oxides also, glucina, when fused with alkaline carbonates, can expel their carbonic acid, of which no other oxide of the composition $R + O$ is capable. Nothing decisive is to be derived from the fact that chloride of glucinum does not combine, like chloride of aluminium, with the alkaline chlorides, as the compounds of the metallic chlorides with each other must be regarded rather as double compounds than as chlorine-salts, in the same sense that oxysalts and sulphasalts are distinguished. Lastly, it is to a certain extent true that the compounds of glucina may be expressed by simpler formulæ if their composition be regarded as $G + O$, and not $2G + 3O$, as the formulæ of the compounds RO in general are more simple than those of the compounds R^2O^3 .

These reasons cannot justify our attributing the composition $G + O$ to glucina; and even the important fact that glucina is capable of decomposing the solutions of ammoniacal salts, although it forms an exception to an otherwise universal law, is not regarded by the author as sufficiently decisive to destroy the force of the other reasons for the adoption of the constitution G^2O^3 .—*Bericht der Akad. der Wiss. zu Berlin*, 1855, p. 581.

On Amylic Alcohol. By L. PASTEUR.

Crude amylic alcohol consists for the most part of two chemically similar bodies, which however are optically distinct. The atoms in the one have a different arrangement from those of the other. One is active in polarized light, the other passive.

The compounds of active amylic alcohol are all active, those of the inactive are also inactive. The proportions in which the two kinds occur together varies according to the mode of preparation of the alcohol. The crude oil produced by the fermentation of the juice of beet-root contains one-third of the active and two-thirds of the inactive alcohol; the crude oil from the fermentation of molasses consists of the two alcohols in nearly equal proportions. The two alcohols cannot be separated by distillation; the author prepared them from the sulphamylate of baryta. A very large quantity of this salt is prepared from the crude oil. The purified crystals exhibit no difference in appearance or chemical composition, but it is soon

seen that a portion of them dissolves $2\frac{1}{2}$ times as easily as the other. The most readily soluble portion contains the compound of the active alcohol, which, when prepared from this compound, rotates the plane of polarization about 20° to the left in a cylinder of 50 centims. in height, whilst that prepared from the less soluble baryta-salt possesses no rotatory power.

These two alcohols are extremely interesting, because we may treat one in the same way as the other, without producing any essential difference. The author has found a difference in the specific gravity. The active alcohol is about one-hundredth heavier than the other. From this it follows that an equal volume of the two bodies cannot contain the same number of atoms. The active boils at $260^\circ.6$ to $262^\circ.4$ F., the inactive at $264^\circ.2$ F. Mixtures of the two boil at intermediate temperatures.

The separation of the two baryta-salts only requires 15 to 20 recrystallizations. The salt of the active alcohol is concentrated in the mother-liquor. The difficulties of the separation lie entirely in the isomorphism of the two salts. Hence the two salts unite in all proportions, and it is only the great difference in their solubility that causes their separation. This isomorphism is exceedingly deserving of notice, because it proves that a dissymmetry may be present and not present in the molecular state of two salts, whilst *à priori* we should conclude that this would constitute an insuperable barrier to the union of the molecules of two salts, so as to crystallize together. The author long supposed that he had to do with two completely different salts of sulphamylate of baryta, until he convinced himself that it was otherwise.—*Comptes Rendus*, xli. p. 296.

On some Saccharine Substances. By M. BERTHELOT.

1. The Australian manna (Manna of the Eucalyptus) contains a crystallizable sugar, which was prepared in 1843 by Johnston, and regarded by him as grape-sugar, $C^{12}H^{12}O^{12} + 2HO$. According to Berthelot's experiments, this is a peculiar kind of sugar, for which he proposes the name of *melitose*.

The reactions of this body agree for the most part with those of cane-sugar. It appears to consist of two isomeric bodies, of which one is capable, and the other incapable of fermentation; the latter must be placed near sorbine.

Melitose, as extracted by water from Australian manna, crystallizes in extremely fine needles; it is about as soluble as mannite, and has a slight sweet taste. It rotates the plane of polarization to the right; its rotatory power (with reference to the transition-colour) is $(\alpha)_D = +88^\circ$. It is therefore about one-fourth greater than that of cane-sugar. When crystallized at the ordinary temperature, melitose has the formula $C^{12}H^{12}O^{12} + 2HO$. At 212° F. it becomes semifluid, and loses 1 atom of water. At 266° F. it loses a fresh quantity of water; at a higher temperature it undergoes a change and becomes yellow, and at a still higher one it diffuses the odour of caramel. When kept at 392° F. with muriatic acid for a long

time, it is converted into a blackish-brown mass. When heated with baryta for some hours to 212° F., it does not acquire colour, and retains its characteristic properties. Melitose does not reduce the copper from the solution of potash and oxide of copper; it only acquires this property by boiling with sulphuric acid. By this means it also loses about a third of its rotatory polarizing power, and when isolated it is uncrystallizable.

In contact with yeast it furnishes alcohol and carbonic acid. Melitose, boiled with sulphuric acid and with baryta at 212° F., also possesses this property. All these properties agree very closely with those of cane-sugar. But during fermentation 100 parts of melitose, $C^{12}H^{12}O^{12} + 2HO$, only furnish 22.2 parts of carbonic acid; 100 parts of grape-sugar, $C^{12}H^{12}O^{10} + 2HO$, give 44.5 parts of carbonic acid, or double the quantity. The fermented fluid contains a saccharine body, which is not acted upon in fermentation. This the author calls,—

Eucalyne.—Its composition, dried at 212° F., is $C^{12}H^{12}O^{12}$. Treatment with sulphuric acid does not render this body capable of fermentation. Melitose furnishes exactly half its weight of eucalyne, as proved by direct experiment. Perhaps also treatment with sulphuric acid only converts half the melitose into the sugar which reduces the copper in the test-fluid.

2. *Pinite*.—The author has received a sugar from M. Bourcier de la Rivière, from California. It is said to be derived from *Pinus Lambertiana*. It collects in concrete masses in hollows in the trees, produced by the Indians by the application of fire to the foot of the tree. The Indians eat this sugar.

The author extracted a crystallizable matter by means of water from the crude substance. This he calls *pinite*. Its composition is $C^{12}H^{12}O^{10}$. It tastes nearly as sweet as sugar-candy. It is readily soluble in water, and nearly insoluble in absolute alcohol, but dissolves a little in boiling ordinary alcohol. Its specific gravity = 1.52. Its right rotation is $(\alpha)_D = +58^{\circ}.6$ (with reference to the transition-colour). Pinite does not reduce the oxide of copper in solution of oxide of copper and potash, even after treatment with sulphuric acid. When precipitated with ammoniacal solution of acetate of lead, it furnishes a compound of the formula $C^{12}H^{12}O^{10} + 4PbO$. It is consequently isomeric with quercite, and is distinguished from that sugar by its crystalline form, its stronger sweet taste, and its great solubility. It is not capable of fermentation.

3. *Sugar from Cider*.—The author has extracted from certain ciders a crystallizable sugar, which is isomeric with mannite. With regard to its crystallization and solubility, it is also identical with mannite.—*Comptes Rendus*, September 1855, p. 392.

On the Production of Palmitic Acid from the Mafurra Tallow.
By MM. d'OLIVEIRA PIMENTEL and J. BOUIS.

The inhabitants of Mozambique give the name of Mafurra tallow to a fatty matter, which they extract by means of hot water from

the seed of a fruit which is but little known in Europe. The simple and æconomical extraction of this vegetable tallow causes it to be used in the preparation of a common soap. The almonds of Mafurra, or probably Mafutra, are covered by a light red envelope, with a black spot in the middle. Each almond weighs about 0·660 grm.; the least pressure is sufficient to detach the envelope, which weighs 0·187 grm., so that the decorticated seed weighs about 0·473 grm. The seeds are about the size of a small cacao-bean; they are flat on the inside and convex externally, and they divide easily into two parts in a longitudinal direction.

Their taste is very bitter, and the different products obtained from them obstinately retain this bitterness. The almond is hard, and when bruised exhales the characteristic odour of cacao; pressure only extracts a very minute proportion of fatty matter from it, and it is necessary to have recourse to boiling water or to solvents in order to extract the whole. The employment of æther or benzine has shown that 65 per cent. of fatty matters may be obtained from the husked seeds, and the cake, which is fit for manure, contains 4·3 per cent. of nitrogen.

With different agents the seeds furnish an extractive matter, a very bitter substance, a product which is strongly coloured by alkalies, &c. The colour of the fatty matter is yellowish, and its odour is that of cacao-butter; it is less fusible than tallow, and boiling alcohol dissolves it in very small quantity. Hot æther dissolves it readily, and deposits it on cooling in small stellate crystals. The alkalies saponify it with a very distinct brown colour, but the greater part of the colouring matter is carried into the alkaline solution. Oxide of lead also converts it into soap, and the glycerine produced by this operation does not exhibit its saccharine character until it has been sufficiently agitated with æther, which removes the bitter matter. The fatty acids arising from the decomposition of the alkaline soaps are crystallized, and composed of a highly-coloured liquid acid, and a solid acid which constitutes 0·55 of the total weight.

The liquid acid forms a mass under the influence of hyponitrous acid, and furnishes a product analogous to claidic acid; by dry distillation it is decomposed into carburets of hydrogen and sebacic acid; with oxide of lead it forms a salt which is soluble in æther; in fact it possesses all the characters of oleic acid.

The solid acid, when pure, is perfectly white and sparkling; its point of solidification is permanent at $320^{\circ}\cdot9$ F., and it then forms a crystalline friable mass; its alcoholic solutions form a mass on cooling. This acid furnishes an ammoniacal salt, which is soluble with the assistance of heat, but insoluble in the cold; its nacreous potash- and soda-salts are decomposed by water; its lead-salt fuses at about 229° F., and afterwards sets into an opaque amorphous mass. The æther which it forms with alcohol is fusible at $75^{\circ}\cdot2$ F., &c. These appear to be all the properties of the æthalic or palmitic acid indicated by MM. Dumas and Stas. Analyses of the acid, of the æther, and of the lead- and silver-salts, showed the composition of the acid to be $C^{32}H^{32}O^4$.

Thus palmitine is furnished in abundance by palm-oil and the Mafurra tallow, the only two vegetable substances which contain it; for we cannot take into the account the grains of coffee, which, according to M. Rochleder, contain it in small proportion.

Experiments of another kind have shown us the extreme facility with which the Mafurra tallow is distilled after saponification with sulphuric acid.

This fatty matter, treated with lime like common tallow, and submitted to cold and hot presses, gave excellent results; but we think that the preference should be given to the former method, unless we can succeed in obtaining the tallow free from colouring matter.

The Mafurra seed is very abundant, and easily collected, in Mozambique, Madagascar and the Isle of Bourbon, which is not unimportant, especially at a moment when the principal substances for lighting are at such a high price. The Mafurra tallow is undoubtedly far superior to palm-oil, both for working and for the amount of solid matter which it yields.—*Comptes Rendus*, Oct. 29, 1855, p. 703.

Note on some Phenomena of Oxygenation and Reduction.

By M. KUHLMANN.

In a preceding note* I indicated the power possessed by resinifiable essential oils of absorbing oxygen from the air, and during the first periods of this absorption of becoming powerful oxidizing agents. This oxidizing power, the energy of which is increased by heat, is also possessed by crude turpentine, and occurs in varnishes.

When the oxygen absorbed has been abstracted from the essential oil, for example when it has served to decolorize a sulphuric solution of indigo, the essential oil again absorbs oxygen, and becomes capable of acting successively upon a great quantity of colouring matter, as is the case in the action of the essential oil upon sulphuric acid. However, in this succession of reactions the essential oil undergoes modifications which require further study.

When a current of oxygen is slowly passed in the cold through a sulphuric solution of indigo, constantly agitated with freshly distilled oil of turpentine, the indigo is very soon decolorized. In contact with the air, and without the direct action of the sun's rays, this result would not be produced for several days.

Tincture of litmus, decolorized by an acid solution of hyposulphite of zinc, acquires a red colour by contact with aerated essential oil; and if the free acid be saturated, the blue colour is reproduced with its original intensity. Essential oil of citron, and other resinifiable or acidifiable oils, act like oil of turpentine; oil of bitter almonds produces the phenomena of oxidation and decolorization in the highest degree.

I have also experimented with nut-oil, one of the fatty oils which is capable of absorbing the most oxygen. The same reaction, it

* Page 434 of the present volume.

appears to me, must be produced with more or less energy by all the fatty oils and fats; the confirmation of this fact would give an equally simple and ready explanation of what takes place in the bleaching of palm-oil, wax, &c., under the influence of oxygenating bodies; the fatty matter serving as an excipient, would convey the oxygen to the colouring matter before this oxygen could be permanently fixed.

There are some carburets which appear to resist the absorption of oxygen; benzine, for example, does not give rise to the above-mentioned phenomena except after long exposure to the air. On the contrary, æther and the alcohols possess the property of absorbing oxygen in variable degrees, and afterwards acting upon colours and oxidifiable bodies before becoming acidified. Æther particularly quickly decolorizes solution of indigo, and precipitates basic sesquisulphate of iron from a solution of protosulphate. In this last operation there is no elevation of temperature as with the aerated oil of turpentine.

Very often, in the reduction of oxygenized bodies, things take place in the same way as we have just indicated with regard to oxidation, except that hydrogen, which most frequently acts as the reducing agent, presents much greater resistance to solution when it is isolated; but its effects are energetically shown when it is combined with some other combustible body. Thus carburetted, and especially sulphuretted hydrogen, act upon vegetable colours, decolorizing them by deoxygenation, and upon metallic salts by reducing them. When hydrogen acts upon some metallic salts, we may suppose that its action is exerted by the aid of the body dissolved in the liquid which sets it free. I have however ascertained that the liquid in the midst of which hydrogen is evolved by the action of dilute sulphuric acid upon zinc, does not reduce chloride of silver; for this purpose it is necessary that there should be a communication between the chloride and the zinc, either direct or by the medium of a conducting body. But if the metallic salt be in solution, the reduction proceeds rapidly; and frequently the reduced body is carried off in combination with the hydrogen, as in the cases of sulphuretted hydrogen, arseniuretted hydrogen, &c.

Must we not attribute to sulphur, in the following circumstances, an action analogous to that of oxygen and hydrogen dissolved, but not yet permanently fixed? When zinc is placed in contact with an aqueous solution of sulphurous acid, and, according to the general opinion, sulphite and hyposulphite of zinc are formed, the liquid acquires a yellow colour, which disappears gradually, in consequence of the formation of insoluble sulphuret of zinc. As long as the yellow colour remains, the decolorizing power of the liquid is infinitely greater than after the deposition of the sulphuret. In this case the sulphur is evidently in a state intermediate between solution and permanent combination, a condition analogous to that of the oxygen in the essential oils or æther.

When the gases act upon the animal economy in respiration, their solubility also, in my opinion, exerts a great influence. Thus

is explained the irritating action of protoxide of nitrogen, which acts partly as free oxygen.

The deleterious action of oxide of carbon, and especially of sulphuretted hydrogen, is explained by the solubility of these gases; it results, independently of their poisonous action, from the abstraction of oxygen from the blood which they produce. The more soluble these gases are, the more energetic is their action, for the lungs at each inhalation deprive the air of the deleterious gas, and thus cause its accumulation.

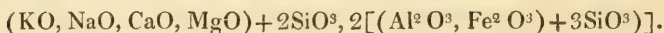
When the hyposulphites remove the oxygen from the aerated essential oils and the hydrocarbons in general, they produce an effect analogous to the action of sulphuretted hydrogen upon the blood.—*Comptes Rendus*, Oct. 8, 1855, p. 538.

Analysis of the Nymphenberg Porcelain, and the Material used there for Saggars. By F. VIELGUTH.

The author treated the mass with carbonate of potash and soda, and obtained the following results:—

		Oxygen.	Proportion of oxygen.	
Silica	72.80	38.59		23.4
Alumina	18.61	8.60	} 9.35	5.7
Oxide of iron	2.50	0.75		
Lime	3.30	0.94	} 1.64	1.0
Magnesia	0.30	0.12		
Soda	1.84	0.47		
Potash	0.65	0.11		

The relation of the oxygen of the bases RO , the bases R^2O^3 , and of the silica approach so closely to the numbers 1 : 6 : 24, that the composition of the Nymphenberg porcelain may be expressed by the formula,—



The mass from which the saggars are prepared in the Nymphenberg manufactory, is also used there in making chemical furnaces, which are very generally diffused in the South of Germany, where they are justly esteemed. 100 parts of the mass (a fragment of a small chemical furnace which had not been used) contained,—

Silica	63.95	Lime.....	0.74
Alumina.....	27.71	Magnesia.....	2.17
Oxide of iron..	4.15	Water	1.25

Vierteljahrsschrift für Prakt. Pharm., iv. p. 553.

On the Action of Water upon certain Sulphomethylates.
By ARTHUR H. CHURCH*.

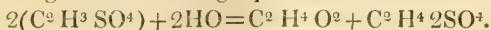
In a former memoir† I have described the products of the action of boiling water upon sulphomethylate of baryta, and more particularly those arising from the spontaneous decomposition of that salt.

* Communicated by the Author.

† Phil. Mag., July 1855.

By further inquiries I have ascertained,—

1st. That sulphate of methyle (which may be considered as the sulphomethylate of methyle) yields with water β -sulphomethylic acid, according to the following equation:—

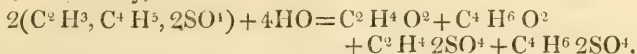


It is possible that the hyposulphomethylic acid, formerly believed to be produced in this reaction, was really β -sulphomethylic acid, which has only recently been recognized.

2ndly. That the decomposition of sulphomethylate of baryta proceeds thus:—



3rdly. That sulphomethylate of æthyle yields with water methylic and æthylic alcohols, together with β -sulphomethylic and parathionic acids; in this way,—



I hope shortly to publish in full the details of my experiments.

On the Composition of Ursone. By Prof. HLASIWETZ.

The author has analysed the substance called *ursone*, recently discovered by Trommsdorff* in the leaves of *Arbutus uva-ursi*. Its composition is $\text{C}^{20} \text{H}^{17} \text{O}^2$. It melts at 388° to 392°F ., and solidifies in a crystalline form. When heated above its melting-point, it remains amorphous and retains water. Analysis gave:—

C	78.35	78.45
H	11.18	11.15
O	10.47	10.40

Sitzungsber. der Akad. der Wiss. zu Wien, xvi. p. 293.

Process for the Formation of a very solid Cement by the action of a Chloride upon Oxide of Zinc. By M. SOREL.

This cement is a basic oxychloride of zinc. It is obtained by suspending oxide of zinc in the liquid chloride of the same metal, or in another chloride isomorphous with chloride of zinc, as in protochloride of iron, manganese, nickel, cobalt, &c. These chlorides may be replaced by muriatic acid.

The cement will be harder in proportion as the chloride is more concentrated and the oxide of zinc heavier. The washed residues of the manufacture of zinc-white, or common zinc-white calcined at a red heat, may be employed; the chloride of zinc should mark from 50° to 60° of Beaumc's areometer. To cause the cement to set more slowly, about 3 per cent. of borax or muriate of ammonia may be dissolved in the chloride, or the oxide may be suspended in water containing a little borax, and afterwards calcined.

The cement thus obtained may be poured into moulds like plaster; it is as hard as marble; cold, moisture, and even boiling water, have no effect upon it; it resists a heat of 572°F . without

* See Chem. Gaz. No. 299. April 1, 1855.

disaggregation, and the most energetic acids attack it very slowly. It is not dear, but its cost might be considerably reduced by mixing metallic, siliceous, or calcareous substances with the oxide of zinc, such as iron or brass filings, iron pyrites, blende, emery, granite, marble, and any of the hard limestones. Soft materials, such as chalk and the ochres, would not do. It will readily receive the brightest and most various colours, so as to be applicable to the formation of mosaics, and other works of great hardness and beauty; some mosaics made of it are already placed in the church of St. Etienne-du-Mont in Paris. It may also be employed in forming moulded objects, such as statues, statuettes, medallions, bas-reliefs, &c. It answers admirably for as a cement, and has been employed for several years by some of the Parisian dentists in stopping decayed teeth.

It may be used instead of oil in painting buildings. For this purpose, pure or coloured oxide of zinc is suspended in water and a little size; this is applied in the same way as the ordinary size-colours, and when as many layers as are desired have been laid on, and the last coat is dry, a little chloride of zinc, of 25° to 30° (Beaumé), is applied with a brush. It may then be pumiced and varnished like oil-paint. This painting is very solid and inodorous; it dries instantaneously, and has the advantage of being antiseptic by virtue of the chloride of zinc.—*Comptes Rendus*, Nov. 5, 1855, p. 784.

Mr. Horsley's *Test for Coffee*.

By J. W. SLATER*.

At the late meeting of the British Association, Mr. Horsley proposed a method of distinguishing coffee from chicory, founded on the fact that decoctions of the former strike an intense brown colour with a solution of the bichromate of potash, whilst decoctions of chicory remain unaffected. So far the test is valuable and accurate. It is open however to two objections. The brown colour depending upon the action of gallic acid, ground acorns and certain kinds of sawdust produce the same results as coffee. Again, roasted corn, beet-root, carrots, &c., being free from gallic acid, will yield a negative result similar to chicory. Although therefore Mr. Horsley's method enables us to distinguish coffee from chicory, and even to estimate their respective proportions, where *no other substance* is present, it would prove dubious if applied to an unknown sample.

Northern Analytical College, Sheffield,
Nov. 14, 1855.

On Ferrum pulveratum. By Prof. WÖHLER.

In preparing the *Ferrum pulveratum* for medicinal use by the process already described by the author, he recommends the employment of the iron obtained with hydrogen from protoxalate of iron.—Liebig's *Annalen*, cxv. p. 192.

* Communicated by the Author.

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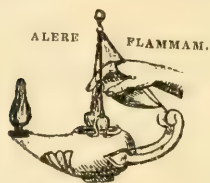
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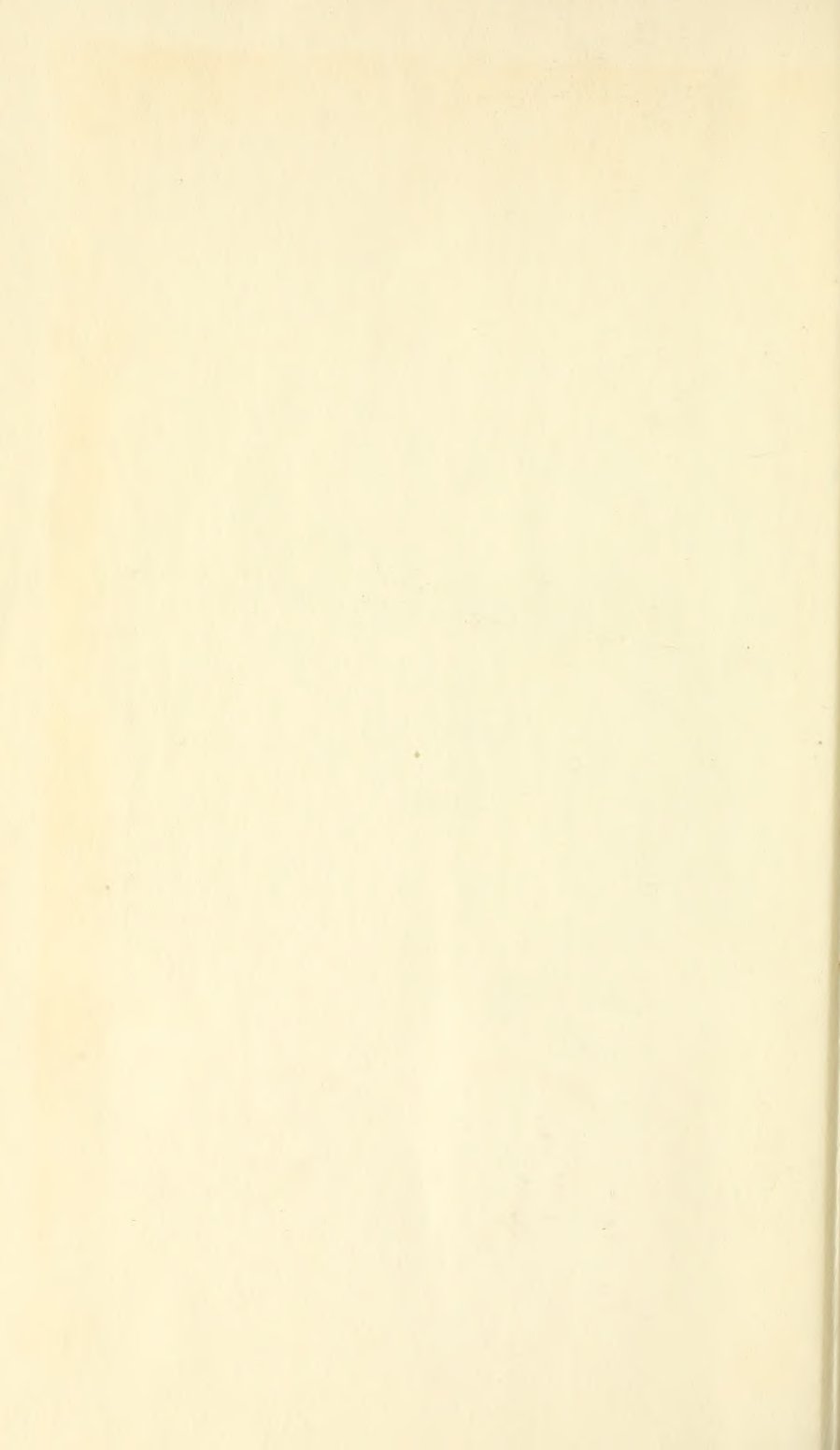
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